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SUMMARY

The ACL-85[®] tape cathodes when activated by acid electrolyte can undergo active chlorine loss by disproportionation to Cl_2 and isocyanuric acid. The extent of loss depends on pH, electrolyte volume, and time of electrolyte contact. Cathode efficiencies in the 70-80% range are obtained using mixed electrolyte ($AlCl_3$, $MgCl_2$ for moderate pH) and minimum electrolyte volume. Chlorine loss does not occur above pH 5.

Salts of trichlorotriazinetrione are much more stable than ACL-85. No significant chlorine evolution occurs when discharged in acid electrolyte, and no capacity loss occurs during tape formulation. Cathode efficienices up to 85% of theoretical (no loss assumed during processing or discharge) were obtained at 0.5 amp/in.[2] in $AlCl_3$ electrolyte. Discharge voltages vs Mg are similar to the ACL-85 system.

The best energy density output to date is 315 watt hours per pound of complete tape cell excluding electrolyte for the system Mg/$AlCl_3$, $MgCl_2$/ACL-85 at 0.5 amp/in.[2] current density. Further improvement can be made only by reducing activity loss during processing and cell activation.

High capacity ACL-85 tapes (10-18 amp-min/in.[2]) were successfully discharged at current densities up to 1 amp/in.[2] vs Mg in mixed $AlCl_3$, $MgCl_2$ electrolytes. Efficiencies ranged from 60-75% at high drain rates.

Fairly flat discharge curves (2.4-2.6 volt vs Mg) were obtained when ACL-compound tape cathodes are discharged at low current densities (0.05 amp/in.[2]) in neutral ($MgCl_2$ and $MgBr_2$) electrolyte. Cell voltage decay at higher drain rates was apparently due to increased resistance caused by electrochemical reaction products.

The full cell system Li/$LiClO_4$, methylformate/ACL-85 or ACL-70[®] maintain 3.0 volts at 0.10 amp/in.[2]. A conventional tape cathode was used. The best coulombic efficiencies obtained for these systems to date are 25% (ACL-85) and 50% (ACL-70).

Initial effort to prepare a high surface area lithium from dispersions and by electroplating were unsuccessful. Dispersed lithium was poorly conductive and highly reactive chemically. Initial electroplating resulted in alloy formation. Further technique refinements are necessary.

Magnesium was found to discharge well in a nonaqueous basic electrolyte system $LiOCH_3$, CH_3OH. Open circuit voltage was -2.2 volt vs NCE and -1.85 volt at 0.1 amp/in.[2].

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF FIGURES

I. INTRODUCTION

A. BACKGROUND

During the first quarter a new tape couple, based on the $Mg/AlCl_3$, HCl/trichlorotriazinetrione (Monsanto ACL-85[R]) system was developed. Static cell output data demonstrated a flat discharge curve with cell voltages above 2.0 volts at current densities close to 1 amp/in.^{2}. Actual cathode coulombic efficiencies above 80% were measured, but output reproducibility was erratic. High energy output ($\approx$300 watt-hours/pound of complete tape cell excluding electrolyte) indicated promise for this system as a potential 200 watt-hour/pound cell.

Both lithium and magnesium were examined as potential non-aqueous system tape anode materials. Lithium was found to work satisfactorily with lithium perchlorate or potassium hexafluorophosphate in methyl formate. Magnesium results were still erratic at the end of the quarter, primarily because of surface preparation problems.

Emphasis during the second quarter was to improve and optimize the Mg/ACL-85 tape system. In addition, the discharge characteristics of active chlorine compounds were to be examined versus lithium and magnesium in nonaqueous tape configuration systems.

B. SECOND QUARTER OBJECTIVES

The specific objectives for this quarter were to:

1. Optimize the energy density output of the aqueous Mg/ACL-85 system and evaluate the complete tape system under dynamic conditions.

2. Determine the performance of active chlorine compounds in nonaqueous electrolyte and start full cell tape configuration studies using a lithium foil anode.

3. Continue screening of selected lithium and magnesium systems in nonaqueous electrolyte using the free electrolyte test cell.

4. Determine the effect of lithium purity and system water content on anode discharge characteristics.

5. Develop a tape configuration lithium anode with a specific effort to produce a high surface area electrode.

6. Produce continuous lengths of ACL-85 tapes.

1

Production of continuous lengths of tape and dynamic evaluation of Mg/ACL-85 tape cells were postponed to completely analyze the causes of ACL compound instability during tape preparation and cell activation. In addition, other ACL salts were evaluated in acidic aqueous electrolyte, and the ability to discharge ACL compound tape cells in neutral electrolyte was investigated. All other objectives were accomplished.

II. TASK I. HIGH ENERGY COUPLE RESEARCH

A. CATHODE RESEARCH AND DEVELOPMENT

1. 2,4,6-Trichlorotriazinetrione and Derivatives in Aqueous Electrolyte

a. Chemical Stability of ACL-85® in Aqueous Electrolyte

During the first quarter, it was found that ACL-85 tapes would lose activity during processing and on standing unless the acetylene black was vacuum dried beforehand. Using pre-dried conductor material, tape cathodes were made that consistantly discharged at 70-80% efficiency in $AlCl_3 \cdot HCl$ electrolyte. Recent discharge data with new batches of electrodes have been erratic, with substantially lower efficiencies in many cases. Investigation has shown considerable active chlorine loss only after contact with certain electrolytes. This phenomenon is illustrated in Table 1 for a typical cathode formulation* containing 65 wt-% ACL-85. Active chlorine analyses were performed on fresh tapes from the same batch and on discharged tapes immediately after passing the cut-off voltage (-1.5 volt vs Mg).

Table 1

ACTIVITY LOSS OF ACL-85 TAPE CATHODES DURING DISCHARGE

Electrolyte - 2M $AlCl_3 \cdot 0.5M$ HCl
Current Density - 0.5 amp/in.^{2}
Anode - Primary Magnesium

Measured Cathode Efficiency %	Active Chlorine Analysis, %	
	Before Discharge	After Discharge
48	91**	10
49	91**	5
48	91**	4

**Based on known amount of active material added initially.

These data are for extreme cases but they do illustrate the possible extent of activity loss. It is apparent that most of the active chlorine reacted during discharge. However, only half reacted electrochemically with magnesium. The other half reacted by another mechanism. The shape of typical discharge curves (Figure 1) for two apparent low efficiency tests illustrates essential cathode depletion at cutoff voltage (1.5 volts).

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* Standard cathode tape formulations contain 2.75 wt-% binder (polyvinyl formal) and 2.75 wt-% fiber (1/4 in. dynel). Active cathode material and acetylene black comprise the remainder.

Cell No.   Current

80414-9   2 A/3 in.²

80414-8   1 A/3 in.²

65 wt-% ACL-85
29.5 wt-% Shawinigan Acetylene Black
2.75 wt-% Polyvinyl Formal Binder
2.75 wt-% 1/4" Dynel Fibers

4 mil Dynel Separator

4 mil Primary Magnesium Anode

Cathode Coulombic Efficiency

Cell Voltage
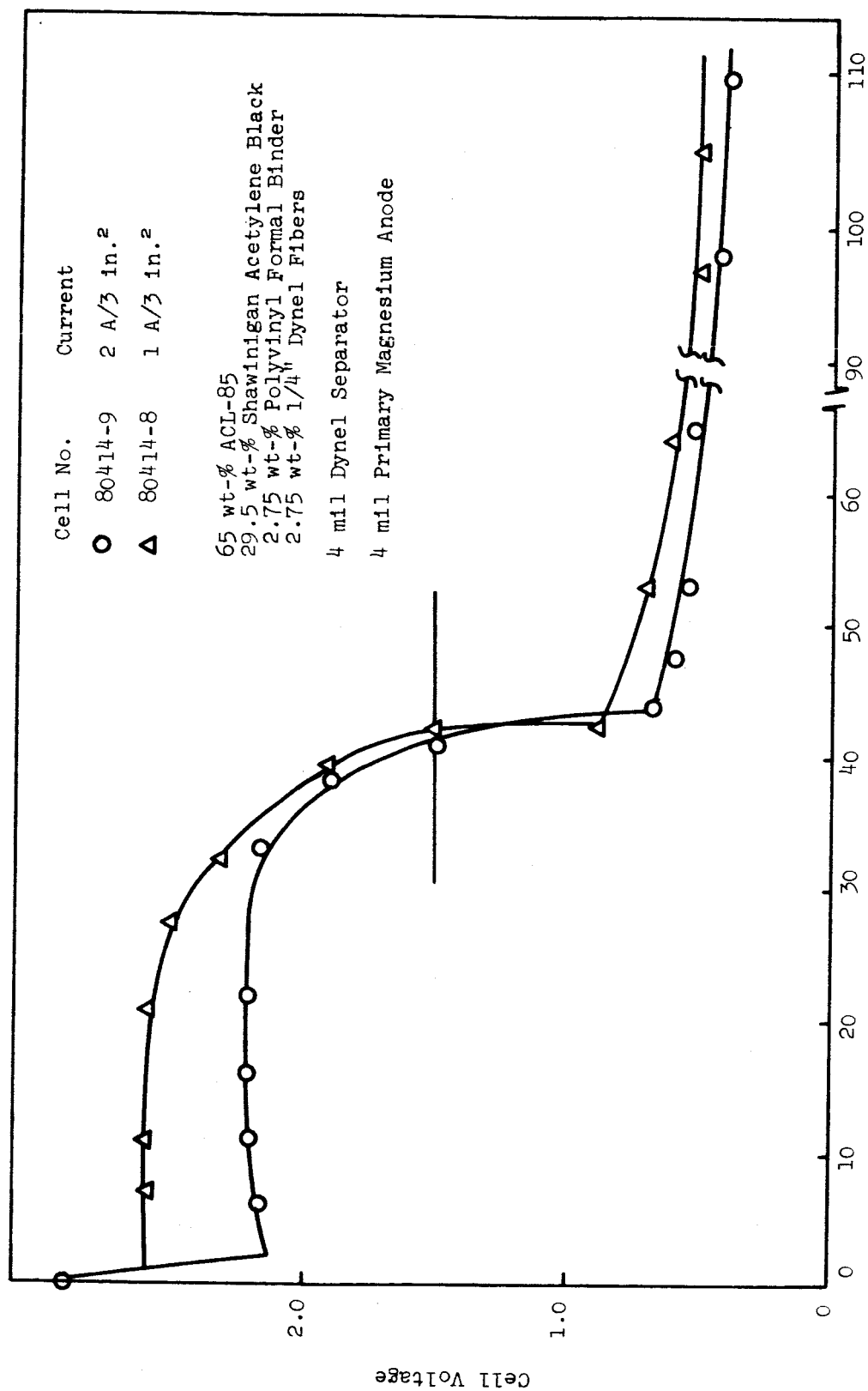
Figure 1. Shape of Mg/ACL-85 Discharge Curve In 2M AlCl₃·0.5M HCl Electrolyte

4

The extent of activity loss varied from test series to test series, but results indicate that this activity loss is peculiar to acid electrolyte. Data in Table 2 show active chlorine loss when fresh tape cathodes are immersed in various electrolyte solutions for five minutes. A typical 65 wt-% ACL-85 cathode formulation was used.

Table 2

EFFECT OF ELECTROLYTE ON ACL-85 TAPE CATHODE ACTIVITY LOSS

Electrolyte Solution	Original Active Chlorine Remaining After Five Minute Soak, %
2M $AlCl_3 \cdot 1M$ HCl	53
2M $AlCl_3 \cdot 0.5M$ HCl	65
1M $AlCl_3 \cdot 0.5M$ HCl $\cdot$ 1M $LiClO_4$	74
2M $LiClO_4$	93
H_2O	95

The activity loss for ACL-85 cathode tapes when activated by acid electrolyte is due to breakdown to isocyanuric acid and chlorine, the reverse of the initial
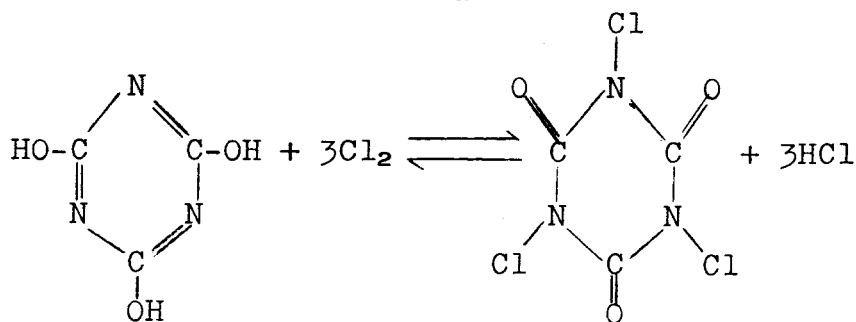
preparative reaction. Table 3 shows the comparative effect of 3 ml of water and various acid electrolytes on the active chlorine content of 0.05-g sample of ACL-85. A strong Cl_2 odor is evident when the strong acid electrolyte solutions are used.

This is a solution reaction and explains the nonreproducibility of previous results. ACL-85 tape cathode disproportionation depends on electrolyte volume, soak time prior to discharge, and the discharge time itself. High rate discharges with minimum electrolyte soak times resulted in high efficiencies.

The best discharge results were obtained by eliminating free HCl as an original constituent and using mixed electrolytes. Elimination of acidic electrolyte completely resulted in poor discharge characteristics, at least at high current densities. Behavior in neutral electrolyte is discussed below. Some typical data in Table 4 illustrate these facts.

5

Table 3

THE EFFECT OF ACIDIC ELECTROLYTE
ON AC1-85 DISPROPORTIONATION

Electrolyte Solution Volume - 3 ml
ACL-85 Sample Weight - 0.05 g
Exposure Time Before Analysis - 5 minutes

Solution	Original Active Chlorine Remaining, %
blank	100
H_2O	100
0.5M HCl	10
2M $AlCl_3$·0.5M HCL	19
2M $AlCl_3$	56
2M $MgCl_2$	90

Table 4

DISCHARGE OF AC1-85 TAPE CATHODES
IN MIXED ELECTROLYTES

Cathode Formulation - Standard 65 wt-% ACL-85 Formulation
Anode - Primary Magnesium
Electrode Area - 3 in.^{2}
Current Density - 0.5 amp/in.^{2}
Approximate Total Capacity - 14-16 amp-min
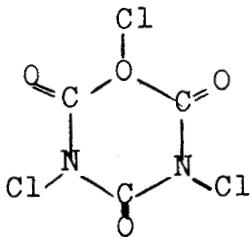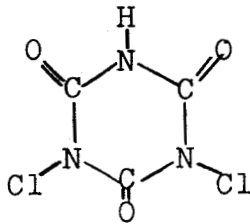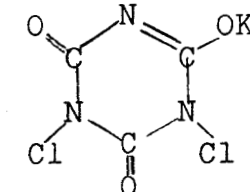
Electrolyte	Cathode Coulombic Efficiency*, %	Average Discharge Voltage, volts vs Mg
2M $AlCl_3$·0.5M HCl	40-60	2.35-2.40
2M $AlCl_3$	64-68	2.20-2.25
1.5M $AlCl_3$·0.5M $LiClO_4$	65-70	2.15-2.20
1.0M $AlCl_3$·1.0M $LiClO_4$	61-68	2.15-2.20
2M $LiClO_4$	~30	~1.7
1.5M $AlCl_3$·0.5M $MgCl_2$	73-77	2.20-2.30
1.0M $AlCl_3$·1.0M $MgCl_2$	70-80	2.15-2.25
2M $MgCl_2$	30-50	~1.90

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* Based on active chlorine content as analyzed
prior to activation.

Even with the best mixed electrolyte systems (AlCl$_3$, MgCl$_2$) there appears to be 10-15% activity loss during discharge based on final active chlorine analysis. In addition, there is also 5-15% activity loss in processing ACL-85 tapes.

Preliminary data with salts of chlorinated triazinetriones indicate they are much more stable than the fully chlorinated material. The various materials being examined are listed in Table 5.

Table 5

DESCRIPTION OF ACL-85 DERIVATIVES

Active Chlorine Compound	Structure	Capacity Amp-min/g
ACL-85		41.5
ACL-70®		32.5
ACL-59®		27.0
ACL-66® (mixed salt of ACL-59 and ACL-85)		30.5
ACL-75® (mixed salt of ACL-59 and ACL-85)		35.0

ACL-85, -70, and -59 are commercially available materials. ACL-66 and -75 are experimental materials supplied by Monsanto Company. Initial results with ACL-59 and ACL-66 show no significant activity loss on processing. In addition, cathode efficiencies up to 85% have been obtained with ACL-66 in AlCl$_3$ electrolyte. No chlorine formation was noted for either ACL-59 or ACL-66.

The discharge voltages are identical to those obtained with ACL-85. Despite lower capacities compared with ACL-85, ACL-66 and -75 may be promising if chemical stability is maintained.

In general, the dichlorotriazinetriones are more stable than the trichloro derivative. The first chlorine of the trichloro compound is very labile and easily hydrolyzed or reduced. The increased stability of the "ACL" salts is reflected in high activity retention after processing (Table 6).

Table 6

ACTIVITY LOSS DURING PROCESSING FOR VARIOUS "ACL" CATHODE TAPES

Formulation: 65 wt-% "ACL" material, 2.75 wt-% polyvinyl formal binder, 2.75 wt-% dynel fiber, 29.5 wt-% acetylene black

Technique: Slurry of cathode mix in trichloroethylene cast on 4-mil dynel tape and vacuum dried.

Active Material	Original Active Chlorine Remaining After Processing,%
ACL-85	89.6 $\pm$2.8% (24 tests)
ACL-75	94.5 $\pm$1.3% (11 tests)
ACL-66	96.5 $\pm$2.1% (17 tests)
ACL-59	98.1 $\pm$1.0% (3 tests)

The activity loss of ACL-85 during tape preparation appears to be caused primarily by the acetylene black. During the first quarter, the beneficial effect of vacuum drying the acetylene black before tape processing was demonstrated. More recent work has shown that ACL-85 can interact with binder (Table 7).

Table 7
THE EFFECT OF POLYVINYL FORMAL BINDER ON ACL-85 ACTIVITY LOSS DURING TAPE PROCESSING

	Original Active Chlorine Remaining After Processing,%
PVF Present	91 $\pm$1 (based on four tests)
No PVF	95 $\pm$1 (based on four tests)

8

Elimination of polyvinyl formal binder coupled with the vacuum drying pretreatment of acetylene black has led to consistent active chlorine retentions of 91-95%. Removal of the binder does not interfere with electrochemical tests, but a new inert binder material will be necessary for satisfactory mechanical properties.

b. Discharge of ACL-85 Tape Cathodes and Derivatives in Aqueous Electrolyte

During the second quarter, work in this area was directed toward improving the energy density output in acidic aqueous electrolyte and determining the feasibility of successful discharge in neutral electrolyte where anode gassing and ACL-85 active chlorine loss does not occur. A complete compilation of static cell discharge experiments is contained in the Appendix (Table A-1). Only selected or summarized data are presented in the following sections.

(1) Discharge in Acidic Aqueous Electrolyte

The shape of the discharge curve for ACL-85 tape cathodes and absence of significant residual active chlorine after cell voltage drop indicates the electrochemical reduction of tri-chlorotriazinetrione in the tape configuration to be highly efficient. Measured efficiencies in aluminum chloride-hydrochloric acid electrolytes are consistently in the range of 75-85%. These figures do not take into account active chlorine loss due to disproportionation of ACL-85 in acid. They are based on as-measured ACL-85 content prior to discharge and, therefore, are corrected for activity loss during processing.

During the first quarter, energy densities of 290-300 watt-hours/pound of dry ingredients were obtained for the Mg/ACL-85 tape system. There are two areas where improvements must be made to increase energy density output to the 350-400 watt-hour/pound (dry ingredients) objective:

(i) Eliminate active chlorine loss on tape processing (possible maximum improvement 10-15%)

(ii) Eliminate active chlorine loss during activation (possible maximum improvement 10%).

Some progress has been made in area (i). Losses during processing have been cut to 5-7% although good reproducibility has not yet been achieved. Two approaches have been explored to reduce active chlorine loss during activation. The first is the use of mixed salt electrolyte with reduction or elimination of free hydrochloric acid. The second involves use of ACL-85 derivatives that are more stable chemically than ACL-85 itself.

The various electrolyte systems examined, together with results obtained, are shown in Table 8. For maximum efficiency, the best mixed electrolyte system is aluminum chloride-magnesium chloride where magnesium chloride concentration is equal to or less than aluminum chloride concentration. Coulombic cathode efficiencies were generally 80% or better. Cell voltages were somewhat lower than those obtained with aluminum chloride-hydrochloric acid electrolyte. Discharge curves for the best cell from each electrolyte series are illustrated in Figure 2.

Using performance data acquired to date, a projection can be made of the ultimate energy density output that can be expected from the Mg/ACL-85 tape system in aqueous acidic electrolyte. The best coulombic efficiencies are obtained with cathode mix containing a maximum of 70 wt-% ACL-85 and a primary magnesium foil anode. A delivered cell voltage of 2.4 volts is obtained at current densities of 0.5 amp/in.^{2} to 0.7 amp/in.^{2}.

Figure 3 shows the energy density output (excluding electrolyte) for a complete tape cell as a function of overall coulombic efficiency and capacity. Overall efficiency includes activity loss during processing and chemical losses during activation. The best energy density obtained to date is 315 watt-hours/pound complete cell excluding electrolyte for cell no. 80482-2. The overall efficiency was 75% including an approximate 10% active chlorine loss during processing. The "X" denoted in Figure 3 represents the best experimental output to date. Energy density increases can be expected through further development in the following areas:

(i) Increase tape capacity from present levels (8-12 amp-min/in.^{2}) to 20-25 amp-min/in.^{2}. Further increases in capacity for this formulation would probably make the tapes too bulky to handle in a practical manner.

(ii) Decrease active chlorine loss during processing. Losses have been held to 5% and further improvements appear likely.

(iii) Active chlorine loss during activation are expected to decrease during dynamic operation since electrolyte contact time is minimized compared with static cell operation.

It would appear that an overall efficiency of 85% is a reasonable goal with ultimate expected energy densities of 350-370 watt-hours/pound of tape cell excluding electrolyte.

The discharge characteristics of higher capacity ACL-85 tape cathode (15-22 amp-min/in.^{2}) are summarized in Table 9.

10

		Capacity amp-min	Electrolyte
O	80439-3	16.3	$1.5M\ AlCl_3 \cdot 0.5M\ LiClO_4$
△	80445-2	15.6	$1.5M\ AlCl_3 \cdot 0.5M\ MgCl_2$
□	80450-4	14.4	$1M\ AlCl_3 \cdot\ 1M\ MgCl_2$

Current 1.5 Amp., Area-3 in.^{2}

O	80450-3	15.1	$2M\ AlCl_3$
△	80455-14	41.5	$1.5M\ AlCl_3 \cdot 0.5M\ MgCl_2$
□	80482-2	25.8	$2M\ AlCl_3 \cdot 0.5M\ HCl$

Current 1.5 Amp., Area-3 in.^{2}
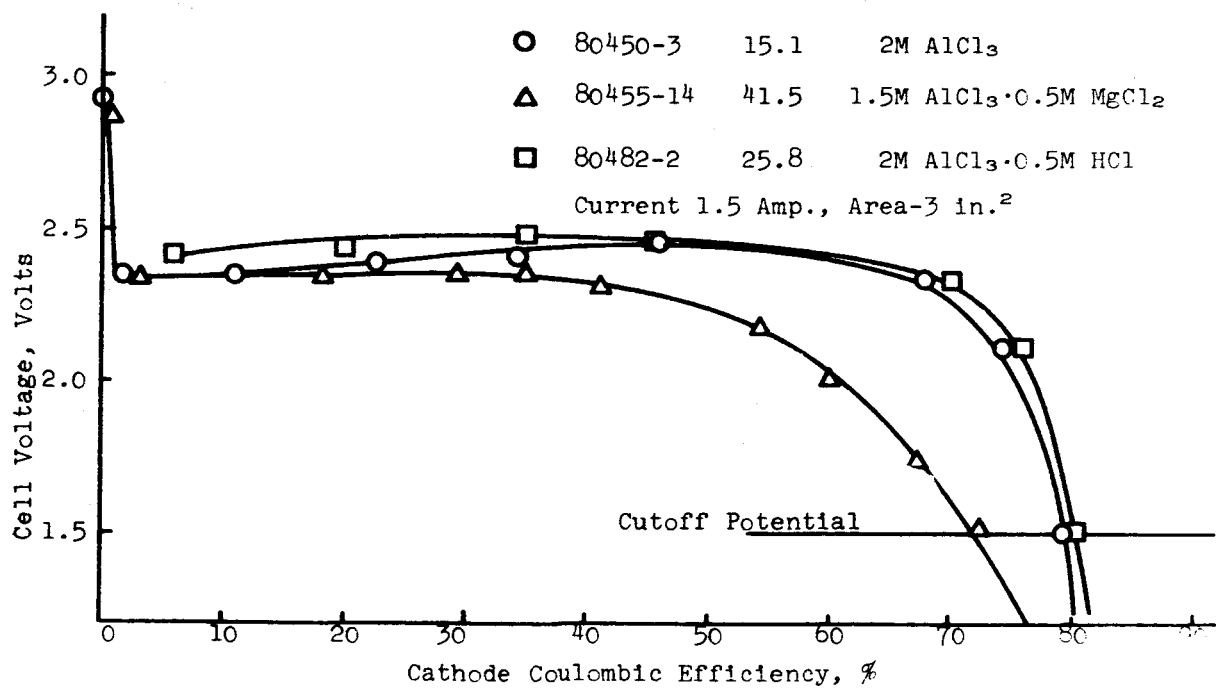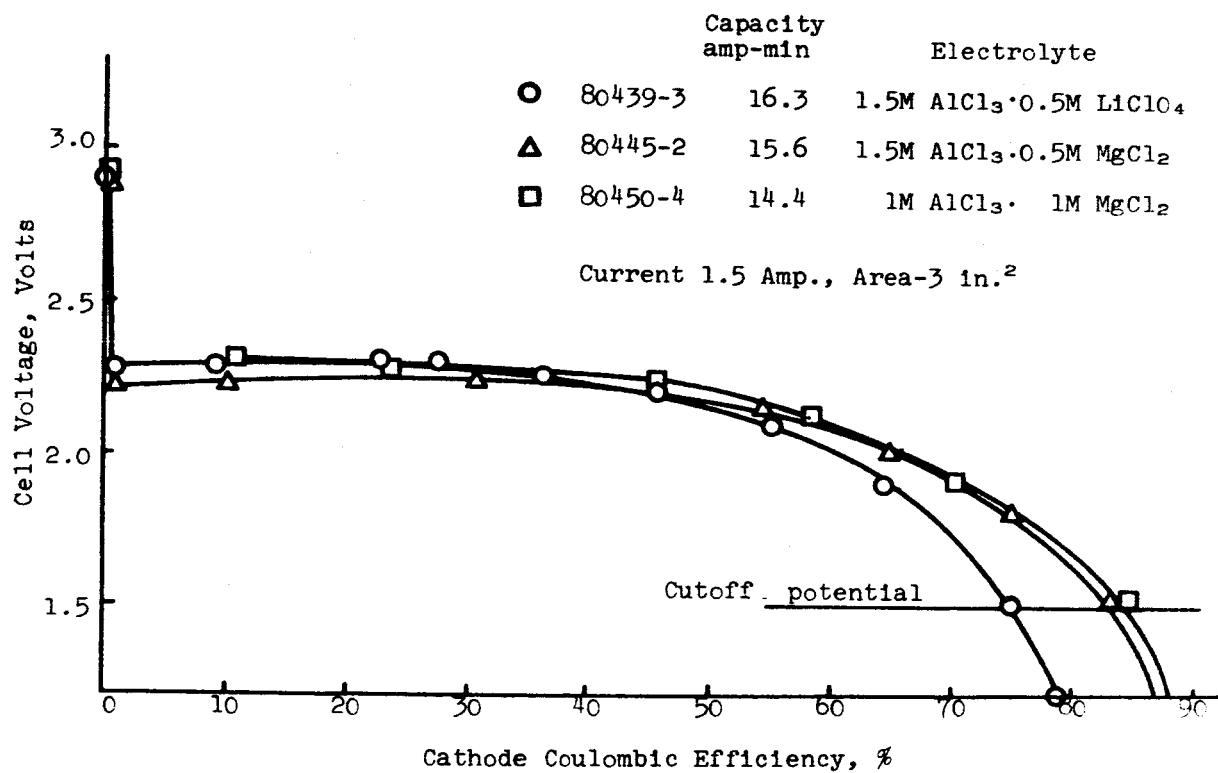
Figure 2. Typical Discharge Data for ACL-85 Tapes in Various Electrolytes, versus Primary Magnesium

11
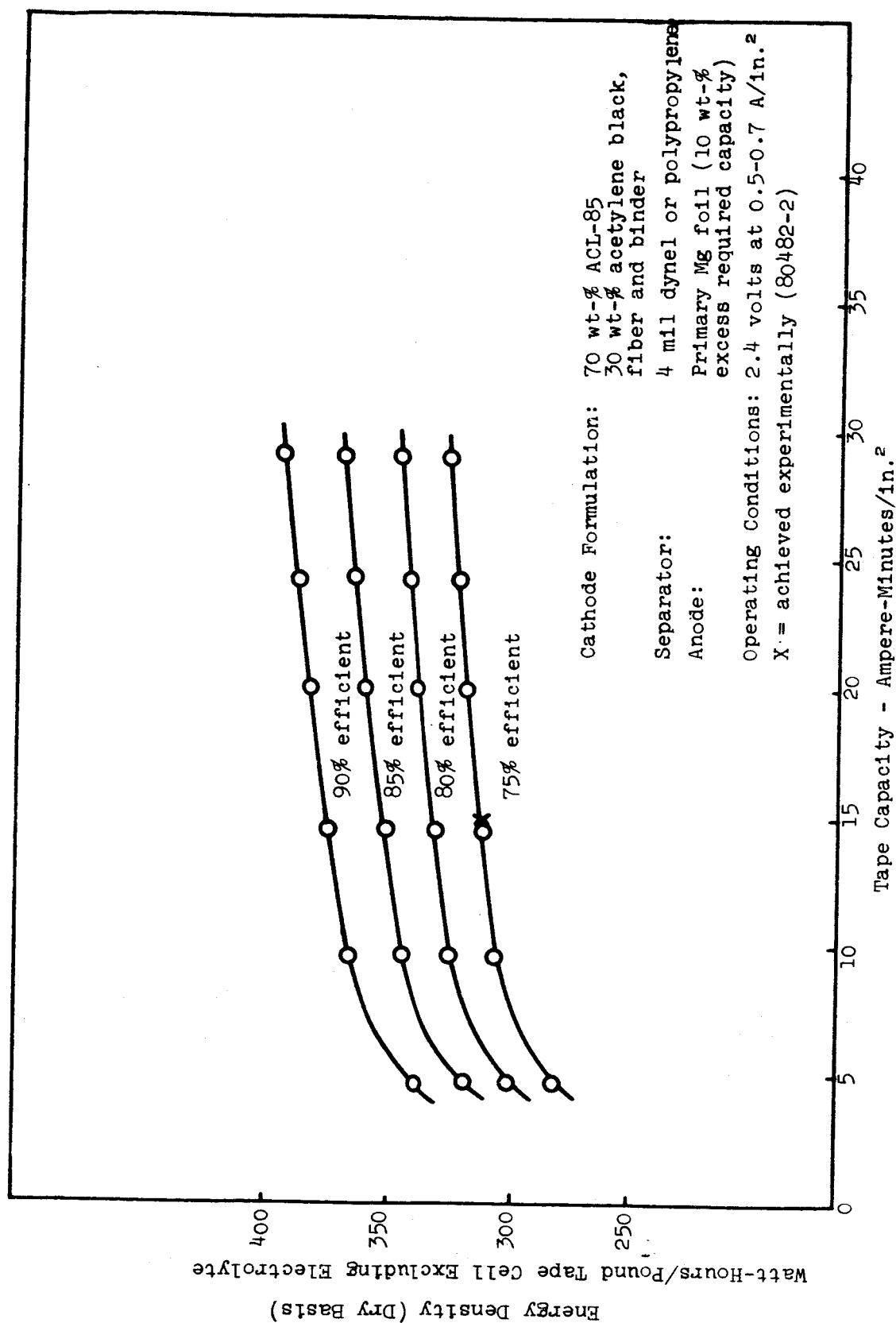
Figure 3. Projected Energy Density Output (Excluding Electrolyte) As a Function of Efficiency and Capacity For The Mg/ACL-85 Tape System

12

Table 8

THE EFFECT OF ELECTROLYTE SYSTEM ON DISCHARGE CHARACTERISTICS
OF Mg/ACL-85 TAPE CATHODE

Cathode Formulation: 65 wt-% ACL-85
                            29.5 wt-% Shawinigan Acetylene Black
                            2.75 wt-% 1/8 in. Dynel Fiber
                            2.75 wt-% Polyvinyl Formal Binder
Separator: 3.5-mil Dynel
Anode: 5-mil perforated primary magnesium
Cell Area: 3 in.^{2}

Cell No.	Electrolyte	Current, amp	Average Voltage, volts	Cathode Coulombic Efficiency (1.5 volt cutoff), %
80442-6	2M $AlCl_3 \cdot 0.5M$ HCl	1.5	2.4	63
80455-16	" "	1.5	2.5	67
80455-14	" "	1.5	2.3	73
80482-2	" "	1.5	2.4	79
80482-3	" "	1.5	2.3	75
80439-2	2M $AlCl_3$	1.5	2.25	72
80450-3	"	1.5	2.35	79
80455-1	1.5M $AlCl_3 \cdot 0.5M$ $MgCl_2$	1.5	2.20	80
80455-2	" "	1.5	2.20	83
80455-4	" "	1.5	2.15	76
80450-1	" "	1.5	2.30	81
80450-7	" "	2.0	2.23	80
80455-15	" "	2.0	2.30	83
80455-11	" "	2.5	2.15	74
80455-20	" "	3.0	2.00	67
80455-12	" "	3.0	1.95	64
80450-4	1M $AlCl_3 \cdot 1M$ $MgCl_2$	1.5	2.20	84
80450-6	" "	2.0	1.90	72
80482-11	2M $AlCl_3 \cdot 0.5M$ $MgCl_2$	1.0	2.50	75
80445-5	0.5M $AlCl_3 \cdot 1.5M$ $MgCl_2$	1.5	1.90	42
80439-3	1.5M $AlCl_3 \cdot 0.5M$ $LiClO_4$	1.5	2.20	75
80439-9	" "	1.5	2.10	70
80442-8	" "	1.5	2.15	73
80442-2	" "	1.5	2.15	71

Table 9

DISCHARGE CHARACTERISTICS OF HIGH CAPACITY (15-22 AMPERE-MINUTES/INCH^2)
Mg/ACL-85 TAPE CELLS IN AQUEOUS ELECTROLYTE

Cell No.	ACL-85 In Cathode Mix, wt-%	Capacity amp-min/in.^{2}	Electrolyte	Current Density amp/in.^{2}	Cathode Efficiency %(to-1.5volts)	Operating Voltage volts
80455-12	65	14	1.5M AlCl$_3$·0.5M MgCl$_2$	1.0	71	1.95
80455-15	"	16	" "	0.7	76	2.30
80455-11	"	17	" "	0.8	82	2.10
80455-14	"	17	" "	0.5	72	2.25
80455-13	"	18	" "	0.8	74	2.15
80463-2	"	19	" "	0.7	62	2.15
80455-20	"	20	" "	1.0	67	2.00
80460-3	70	20	" "	0.7	78	2.20
80460-8	"	20	" "	0.5	59	2.20
80455-17	65	18	1.5M AlCl$_3$·0.5M MgCl$_2$·0.2M HCl	0.7	77	2.20
80455-18	"	20	1.0M AlCl$_3$·1M MgCl$_2$·0.2M HCl	0.5	73	2.25
80460-5	70	21	1M AlCl$_3$·1M MgCl$_2$	0.7	54	2.10
80455-19	65	18	" "	0.7	54	2.10
80455-10	65	17	2M AlCl$_3$·0.5M HCl	0.8	56	2.30
80455-16	"	17	" "	0.5	71	2.50
80463-9	"	18	" "	0.7	59	2.25
80460-1	70	19	" "	0.7	55	2.20
80460-6	"	22	2M AlCl$_3$	0.7	57	2.25
80463-4	65	20	"	0.5	52	2.10

In general, increasing capacity, at least up to 20 amp-min/in.^{2} does not markedly change the discharge characteristics. As expected, the heavier tapes maintain slightly higher voltages at high current drains. Representative discharge curves are illustrated in Figure 4.

The discharge characteristics of the various salts of ACL-85, ACL-59, ACL-66, and ACL-75 (see Table 5), were screened in various acidic aqueous electrolytes. The results are summarized in Table 10. A comparison of the four systems is illustrated in Figure 5.

The ACL-59 tapes ran poorly, with cathode efficiencies no higher than 50%. Since there is no activity loss during tape preparation, poor efficiencies may be due to high solubility (9 g/100 g H_2O at 20°C). Because of poor performance and relatively low capacity, ACL-59 was eliminated from further consideration.

The polarization characteristics of ACL-66 and ACL-75 are similar to those for ACL-85. Because of better chemical stability, these mixed salts exhibit better overall cathode efficiencies. ACL-66 shows no activity loss during processing with the result that overall efficiencies as high as 85% were obtained. ACL-75 exhibited slightly lower efficiencies (65-71%), which directly reflect the 5-8% activity loss during processing. As with the ACL-85 tape cathodes, the aluminum chloride-magnesium chloride solution appears to be the best electrolyte system.

The ability to discharge ACL-85 cathode successfully in neutral electrolyte is highly desirable. Elimination of the acidic electrolyte would avoid anode gassing and activity loss due to cathode decomposition. Initial work, during the first quarter, showed that ACL-85 tape cathodes exhibit steadily increasing polarization during discharge in neutral electrolyte. Further work was carried out to clarify the nature of this polarization and determine under what conditions, if any, a neutral electrolyte system could be used successfully. Discharge data indicate that polarization is caused by the accumulation of an electrochemical discharge product rather than a chemical decomposition product. Contact of ACL-85 tape cathodes with various neutral electrolyte systems for varying periods of time resulted in no significant activity loss. As illustrated in Figure 6, polarization is related to discharge time rather than elapsed time after activation. Current shut-down during a run has no effect upon ultimate efficiency or polarization. Extending the discharge time by decreasing the current actually improves output (Figure 7) with no loss in efficiency.

Indications are that ACL-85 and "ACL-salts" can be discharged successfully in neutral electrolyte at low current densities. Typical results are shown in Table 11.

15
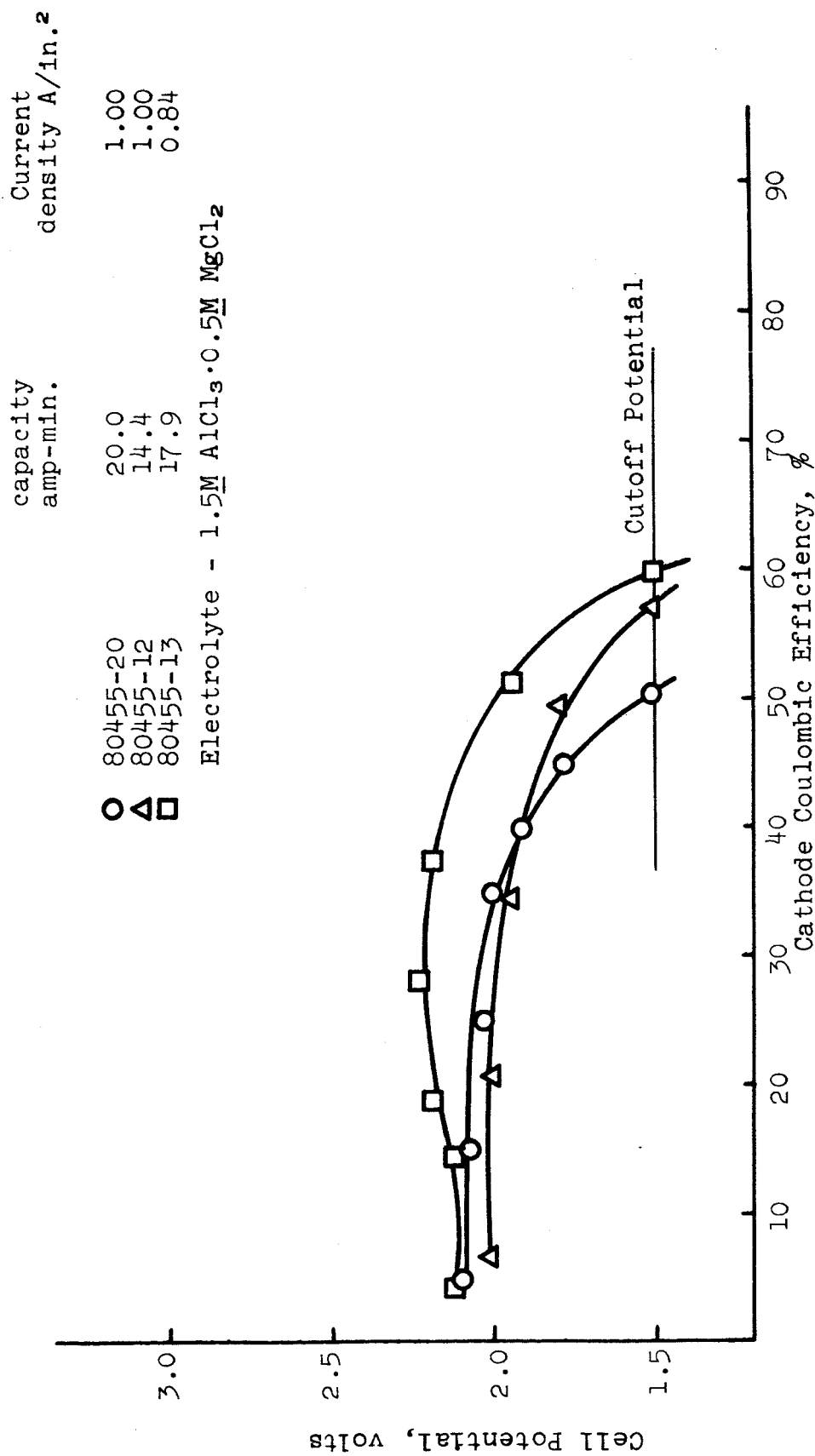
Figure 4. Representative Discharge Curves of ACL-85 Cathode Tapes of Various Theoretical Coulombic Capacities
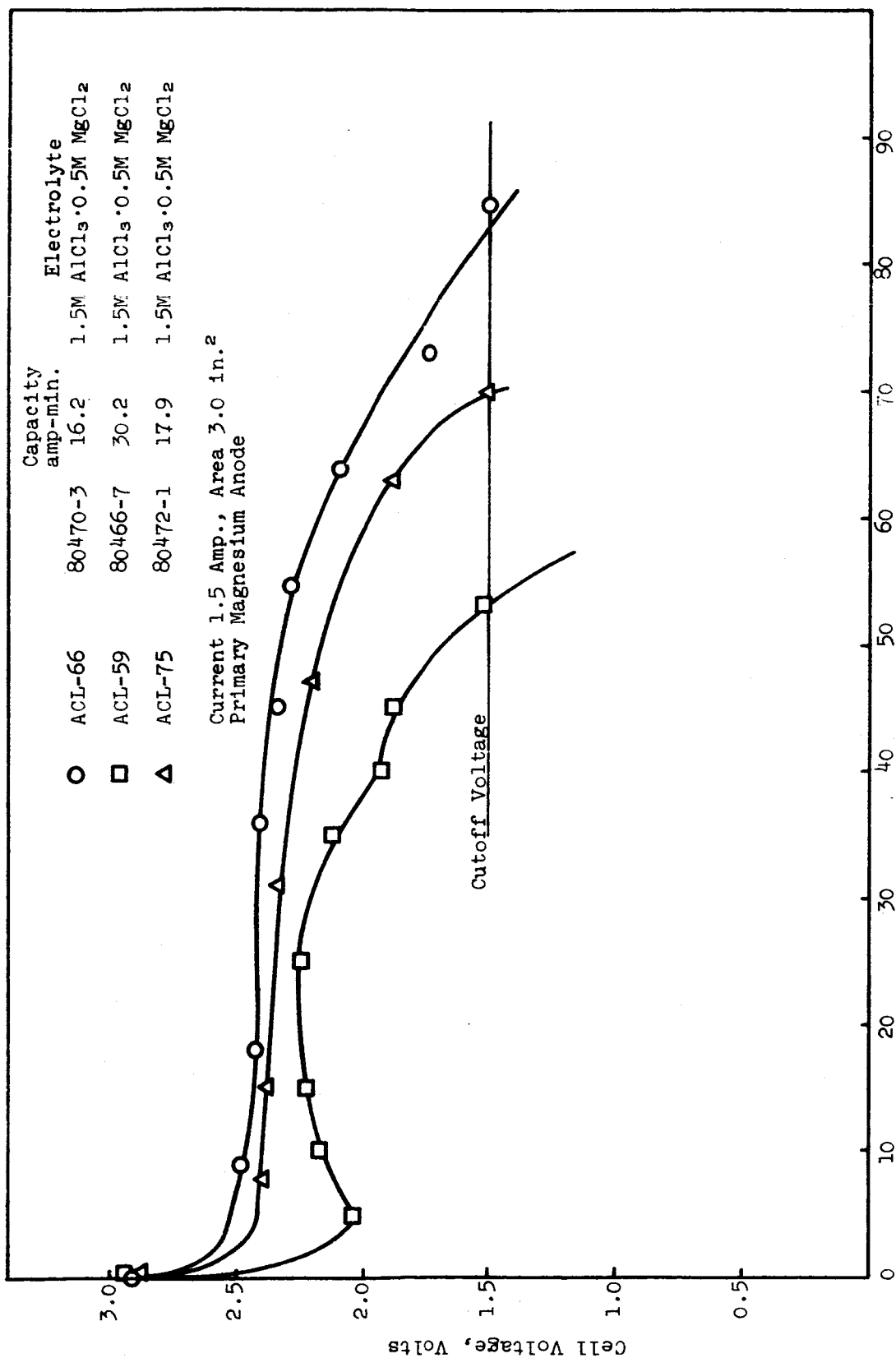
Figure 5. Typical Discharge Data For ACL-59, ACL-66 and ACL-75 Versus Primary Magnesium

Table 10

DISCHARGE CHARACTERISTICS OF "ACL" SALT TAPE CELLS IN ACIDIC
AQUEOUS ELECTROLYTE

Cathode Formulation: 65 wt-% "ACL" salt, 30 wt-% acetylene black, 2.5 wt-% carbon fibers (1/8 in.),
2.5 wt-% polyvinylformal binder

Separator: 4-mil dynel

Anode: 5-mil perforated primary magnesium

Cell Configuration: 3 x 1 in.

Cell No.	Capacity amp-min	Capacity Loss During Processing %	Electrolyte	Cathode Efficiency to 1.5 volts %	Current I amp	Operating Voltage, volts
ACL-75 (35 amp-min/g capacity)						
80483-1	18	8	1.5M $AlCl_3 \cdot 0.5M$ $MgCl_2$	66	1.5	2.15
80472-1	20	8	" "	70	1.5	2.30
80472-2	25	5.5	2M $AlCl_3$	71	1.5	2.35
80472-3	20	5.5	2M $AlCl_3 \cdot 0.5M$ HCl	65	1.5	2.35
ACL-66 (30.5 amp-min/g capacity)						
80470-3	17	0	1.5M $AlCl_2 \cdot 0.5M$ $MgCl_2$	85	1.5	2.35
80486-4	14	0	" "	67	1.5	2.30
80486-2	31	0	" "	68	1.0	2.40
80474-8	21	0	" "	82	1.5	2.30
80474-9	28	0	" "	63	3.0	2.00
80486-3	31	0	1.5M $MgCl_2 \cdot 0.5M$ $AlCl_3$	70	1.0	2.00
80470-1	15	0	2M $AlCl_3$	70	1.5	2.30
80484-5	19	0	"	75	1.5	2.10
80474-2	29	0	"	72	3.0	2.00
80470-2	21	0	2M $AlCl_3 \cdot 0.5M$ HCl	67	1.50	2.35
80474-1	24	0	" "	53	3.00	2.00
ACL-59 (27 amp-min/g capacity)						
80466-7	31	0	1.5M $AlCl_3 \cdot 0.5M$ $MgCl_2$	53	1.5	2.10
80466-10	31	0	" "	51	1.5	2.00
80466-4	22	0	2M $AlCl_3 \cdot 0.5M$ HCl	46	1.5	2.20

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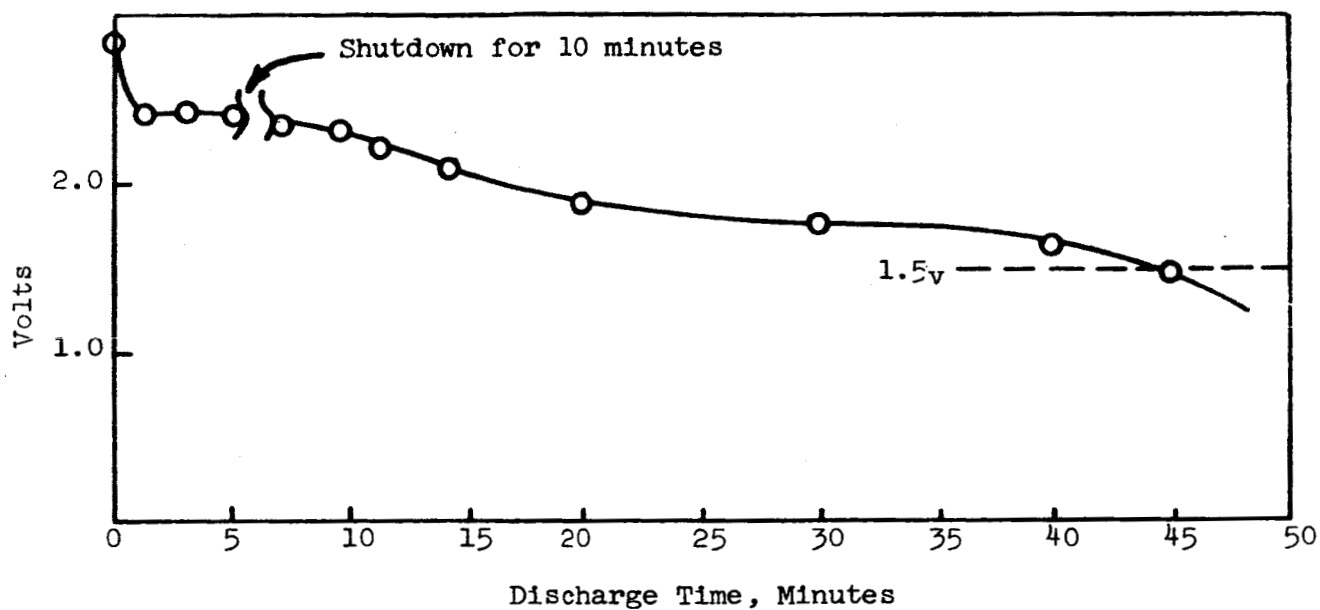
Figure 6. The Effect of Mid-discharge Shutdown on Discharge
of Mg/2M MgCl$_2$/ACl-85 System at 0.17 amp/in.^{2}
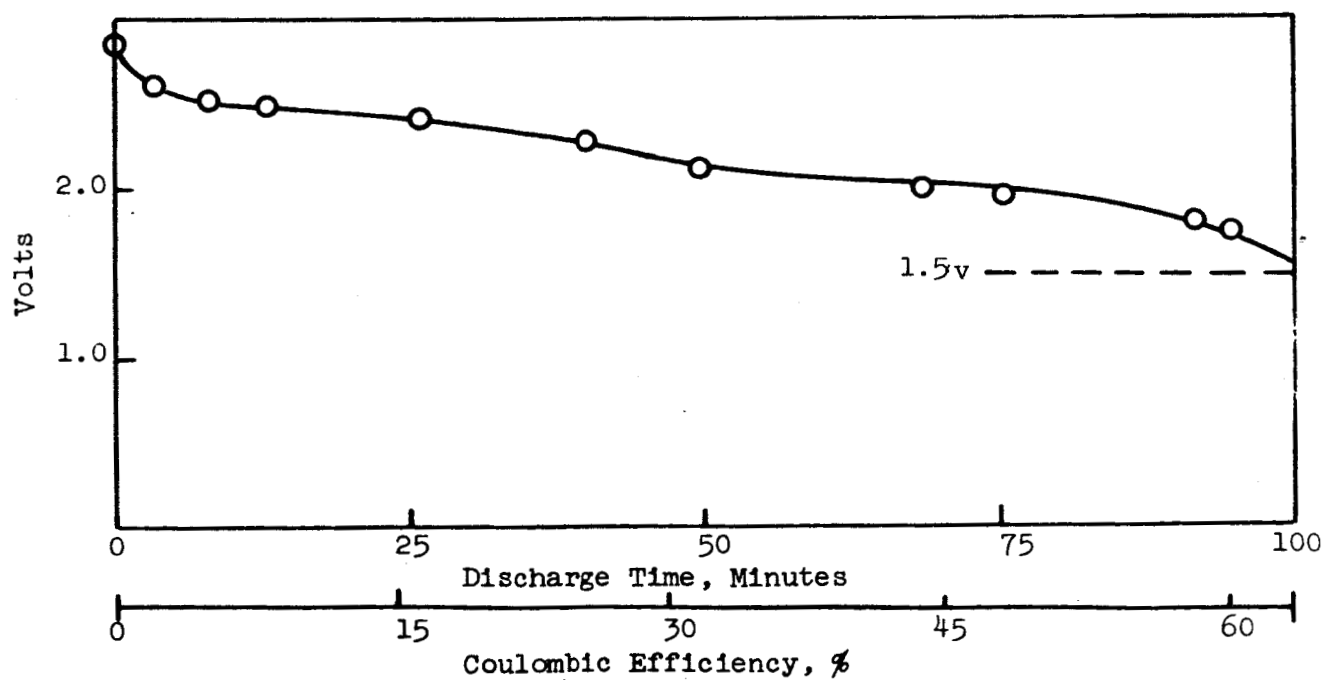
Figure 7. Discharge of Mg/2M MgCl$_2$/ACl-85 System at 0.05 amp/in.^{2}

Table 11

THE EFFECT OF LOW CURRENT DENSITIES ON DISCHARGE CHARACTERISTICS
OF ACL-85, ACL-75 AND ACL-66 TAPE CATHODES
IN NEUTRAL ELECTROLYTE

Cathode Formulation: 65 wt-% ACL compound, 30 wt-% acetylene black, 2.5 wt-% carbon fiber (1/8 in.),
2.5 wt-% polyvinyl formal binder

Separator: 4-mil Dynel

Anode: 5-mil perforated primary magnesium

Cell Configuration: 3 x 1 in.

Cell No.	Capacity amp-min.	Electrolyte	Cathode Efficiency to 1.5 volts %	Current, I amp	Operating Voltage volts
			ACL-85		
80477-6	27	2M $MgBr_2$	63	0.5	1.90
83804-3	11	"	60	0.15	2.10
80482-10	14	"	68	0.15	2.10
80482-7	22	2M $MgCl_2$	75	0.5	2.00
80450-8	11	"	54	0.5	1.80
80463-5	44	"	56	0.5	1.80
80455-1	25	"	59	0.15	2.00
			ACL-75		
80483-9	19	2M $MgBr_2$	75	0.15	2.20
80483-10	20	2M $MgCl_2$	77	0.50	1.90
			ACL-66		
80474-6	22	2M $MgBr_2$	70	0.50	2.00
80488-1	20	"	72	0.15	2.20
80486-5	28	"	75	0.15	2.20
80484-1	18	"	71	0.15	2.20
80474-11	24	2M $MgCl_2$	71	0.50	1.70
80484-3	20	"	53	0.50	2.0
80486-5	28	"	78	0.15	1.85

The mixed salts, ACL-66 and ACL-75, appear to give better efficiencies and cell voltages than ACL-85. In addition, substantially higher voltages are obtained with 2M $MgBr_2$ compared with 2M $MgCl_2$ for all cathode systems studied.

2. 2,4,6-Trichlorotriazinetrione and Derivatives in Nonaqueous Electrolyte

a. Full Cell Preparation

The solubility of organic N-chlorine compounds in typical organic electrolyte systems makes the free electrolyte half-cell screening technique unsuitable for most ACL cathodes. Hence, most of the cathode research has been done using tape configuration full cells with lithium as the working anode. The lithium potential is read separately (vs NCE) so that cathode and anode polarizations can be separated.

In the early experiments the lithium anode was prepared from the same lithium used for half-cell tests. This anode was prepared by slicing block lithium (Fisher), sealing the slice in polypropylene in the drybox, pressing it to a foil in a Carver press at 10,000 psi outside the drybox, followed by unsealing the enclosed foil back in the drybox.

The full cell construction and cathode formulations were similar to those for the aqueous system with the following variations. The static test sandwich type cell was made of polypropylene. Cathode formulations used carbon fibers rather than dynel and polypropylene separators were used. These variations were necessary to insure stability of materials in various organic solvents. A 65% depolarizer content was used unless otherwise noted.

The polypropylene separator offers no resistance problems in the methyl formate system. This was shown by half cell tests of the $Li/KPF_6(MF)$ system in which essentially identical results were obtained with and without a polypropylene separator covering the lithium anode. Some of this preliminary data using this system is shown in Table 12.

These initial polarization data indicated that a Li/ACL-85 tape configuration system could maintain a substantial discharge voltage at reasonable current drains.

b. Full Tape Cell Screening Tests of Various Cathode Types in Nonaqueous Electrolytes

Screening experiments were carried out to test a variety of cathode materials in the full cell configuration and served as an introduction to the more detailed work with the ACL compounds.

21

Table 12

FULL CELL DATA

Test No.	System	Area, in.²	Voltage at Various Currents (ma)												Principle Cause of Failure	Notes
			0	5	10	20	40	60	80	100	200	300	450	600		Some
1	Li/LiClO₄(BL)/AgCl	1 in.²	2.95	2.6	2.3	1.6	1.3	0.85	0.55						Anode (cathode loss)	
2	Li/LiClO₄(MF)/AgCl	1 in.²	2.9	2.3	1.9	1.7	1.9	1.6							Cathode	Addn. of electrolyte improves
3	Li/LiClO₄(MF)/ACL-85	1.5 in.²	4.05	3.95	3.9	3.85	3.7	3.6	3.55	3.5	3.2	2.95			Anode	>2.0 volts for 8 min at 0.2 A/in.²
4	" "	2.0 in.²	4.00	3.95	3.9	3.85	3.75			3.5	3.2	3.0			Anode	
5	Li/KPF₆(MF)/AgCl	1 in.²	3.0	1.4	0.15										Anode and Cathode	
6	Li/KPF₆(MF)/ACL-85	3 in.²	4.1	4.0	3.95	3.85	3.7	3.6	3.5	3.45	3.05	2.8	2.55	1.95	Anode and Cathode	

The results of these experiments are given in Table 13. It is evident from the data that the lithium anode operated effectively in the electrolytes tested. The electrolyte choices were drawn primarily from the half-cell screening data.

Three N-chloro- compounds were chosen for current-voltage screening in methyl formate. One inorganic active chlorine compound (LiOCl) was chosen, and two silver salts were tested (AgCl and AgO).

The N-halogen compounds normally exchange Cl for H upon reduction. However, in non-protonic solvents it may be possible to substitute Li for H when reducing N-halogen acids such as ACL-85 and ACL-59. For example:

$$\text{(hexachloro structure)} + 3\ Li^+ + 6e \longrightarrow \text{(trilithium structure)} + 3\ Cl^-$$
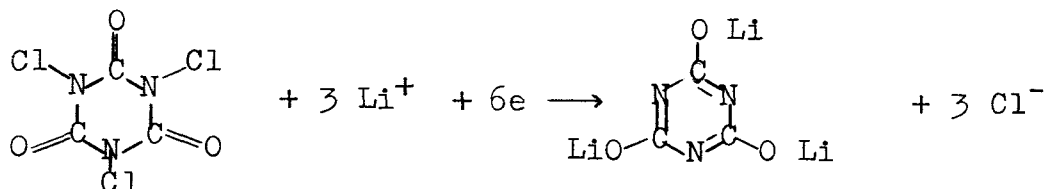
Hence, we postulate that hexachloromelamine did not discharge effectively because this compound cannot accept lithium in place of hydrogen. The amine hydrogen is not acidic.

Other active chlorine compounds that could discharge in nonaqueous solvents are halogen addition compounds (e.g. pyridine perbromide) and N-halogen compounds that discharge to give further unsaturation or coupling (e.g. N,N'-dichlorobenzoquinone-diimine (ref. 1). Some of these will be tested next quarter.

Figure 8 shows the current-voltage discharge data of ACL-85 in methyl formate. $LiClO_4$ and KPF_6 are shown to be equally effective as electrolyte salts. Water appears to decrease the full cell voltage. This loss is due to cathode polarization.

Of the inorganic active chlorine compounds, LiOCl is of interest for nonaqueous solvents (ref. 2). Two samples of LiOCl were tested in tapes prepared similarly to the ACL tapes. The commercial grade of LiOCl (Lithium Corporation of America) included stabilizers and was 25% LiOCl. The K and K Chemical sample also assayed at 30% LiOCl by the iodine-thiosulfate titration method. Both samples discharged similarly in $LiClO_4$(MF). There was considerable activity but very little capacity in these tapes. A tape was discharged in LiCl(DMF) in an attempt to obtain more capacity since one of the products, LiCl, is soluble. The instability and insolubility of the LiOCl is presumably most of the problem, because the discharge in DMF showed no improvement.

Table 13

CURRENT-VOLTAGE DATA ON DISCHARGE OF VARIOUS NONAQUEOUS TAPE CELL BATTERY SYSTEMS

Ref.	System	Cell Voltages at c.d. in amp/in.²									Anode Potential vs NCE at c.d. in amp/in.²								
		0.0	.005	0.01	0.02	0.03	0.05	0.10	0.15	0.20	0.0	.005	0.01	0.02	0.03	0.05	0.10	0.15	0.20
897	Li/LiClO₄(MF)/ACL-85	4.05	3.95	3.80	3.70	3.60	3.30	2.90	2.65	2.30	3.00	3.00	3.00	3.00	2.90	2.80	2.70	2.60	2.60
897	Li/KPF₆(MF)/ACL-85	4.00	3.95	3.85	3.70	3.45	3.20	3.0	2.30		3.05	3.00	2.95	2.90	2.65	2.45	2.40	2.20	
312	Li/LiClO₄(MF)/ACL-59	3.90	3.40	3.10	2.65	2.45	2.20	2.40	2.0	1.2	3.00	2.80	2.75	2.70	2.60	2.60	2.70	2.60	2.50
891	Li/LiClO₄(MF)/HCM*	2.85	2.40	1.80	1.20	0.9	0.4				2.20	2.20	2.20	2.15	2.05	1.95			
860	Li/LiClO₄(MF)/AgCl	2.9	1.8	1.8	1.6						3.15	3.10	3.00	2.90					
323	Li/LiClO₄(MF)/AgO	3.6	2.9	2.7	2.2	1.8	1.55	1.05	0.90		3.05	3.00	2.95	2.90	2.85	2.80	2.75	2.65	
316	Li/LiClO₄(MF)/LiOCl	3.90	3.85	3.75	2.80	2.30	1.80	1.25			3.05	3.05	3.05	3.05	3.00	2.95	2.85		
321	Li/LiCl(DMF)/LiOCl	3.50	3.10	2.85	2.50	2.00	1.30	0.20			3.15	3.15	3.15	3.15	3.10	3.05	3.00		
324	Li(Hg)/LiOMe(MeOH)/ACL-85	3.00	2.80	2.60	2.40	2.10	1.80	0.70			2.20	2.00	1.80	1.60	1.40	1.00	0.00		
328	Mg/LiOMe(MeOH)/ACL-85	2.75	2.55	2.35	2.10	1.70	1.00				2.00	2.00	2.00	1.95	1.85	1.60			
328	Mg/LiOMe(MeOH)/ACL-59	2.50	.20	2.10	1.85	1.60	1.10				2.05	2.00	1.90	1.75	1.55	1.25			
885	Mg/AlCl₃(AN)**/ACL-85				2.80		2.60	2.45		2.05	1.95		1.75		1.60	1.50			1.10

*   hexachloromelamine
** acetonitrile

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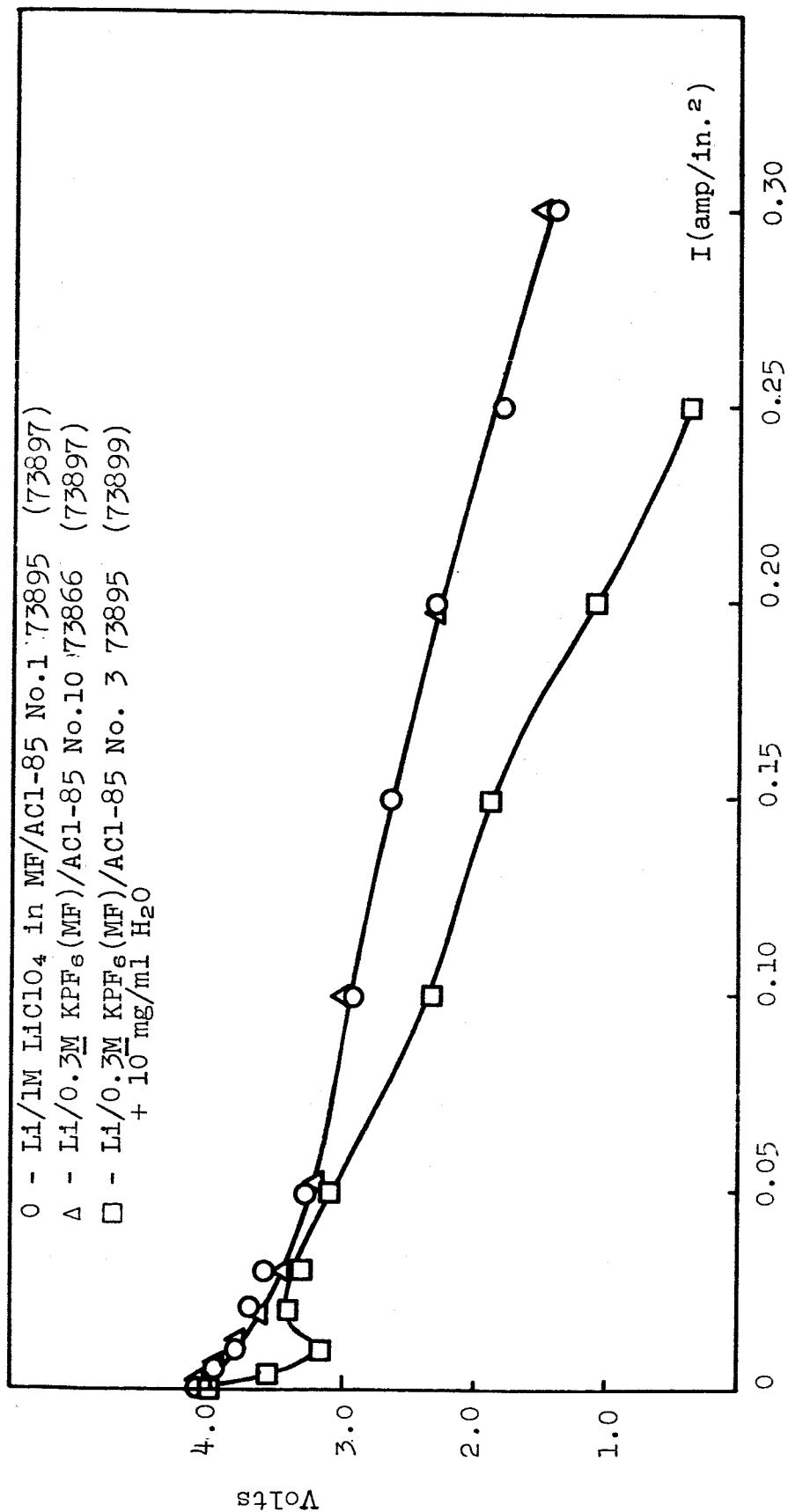
Figure 8. Effect of Electrolyte Salts and of H_2O on Current-Voltage Data for Li/Methyl Formate/ACl-85 Systems (Area = 3 in.^{2})

O – Li/1M LiClO$_4$ in MF/ACl-85 No.1 73895   (73897)
△ – Li/0.3M KPF$_6$(MF)/ACl-85 No.10 73866   (73897)
□ – Li/0.3M KPF$_6$(MF)/ACl-85 No. 3 73895   (73899)
    + 10 mg/ml H_2O

I(amp/in.^{2})

Volts

Since a good discharge has been shown for AgO (ref. 3) in nonaqueous batteries, tapes were made for this program by a method developed previously in this laboratory (ref. 4). The discharge of this tape in LiClO$_4$(MF) showed considerable initial voltage loss and was much less active than the active chlorine compounds. The AgCl data was collected early in the quarter and the cathode was produced by reducing a Yardney Silcad AgO (YS10) cathode and re-oxidizing it in HCl(aq). The data is given in Table 13 for comparison and completeness.

One test was performed on an amalgamated Li anode. This electrode was prepared by wetting lithium with mercury and then annealing the anode at 135°C in vacuum. The anode was indeed deactivated (50/50 wt-% Li/Hg). The result indicates that more work could be done in this area. For example, at 50/50 wt-%, a more active electrolyte than LiOMe(MeOH) could be used. Amalgamation by inclusion of Hg^{++} in solution might also be possible.

Full cell data was also obtained for ACL compounds with magnesium anodes in LiOMe(MeOH) and in AlCl$_3$ (AN). ACL-85 discharged readily against magnesium in AlCl$_3$ and reasonably well in LiOMe(MeOH). From Figure 9 it would appear that the polarization is mostly IR-loss in the AlCl$_3$(AN) system. A constant current discharge (Figure 10) exhibited a flat discharge potential at 2.5 volts but a cathode efficiency of only 25%.

c. Discharge of ACL-Compound Tape Cathodes in Nonaqueous Electrolyte Systems

Emphasis this quarter was placed on the discharge of ACL-compounds versus lithium in methyl formate, since such cells have a large theoretical energy capacity, and have been shown to discharge at drain rates of 0.1 amp/in.^{2} in methyl formate.

The solubility of ACL-85 in methyl formate had been found to be less than in the other nonaqueous solvents used. The addition of salt might be expected to decrease the solubility. However, the solubility increases greatly with addition of LiClO$_4$. Thus, 2.2 g of ACL-85 dissolves in 100 ml of MF. However, more than 20 g of ACL-85 dissolves readily in 100 ml of 1M LiClO$_4$ (MF). In KPF$_6$(MF), the solubility of ACL-85 is not noticeably increased. In γ-BL and EF the addition of LiClO$_4$ also increases the ACL-85 solubility. Active chlorine analysis on the LiClO$_4$ (MF) solution showed almost no loss of active chlorine, even though there was no solid phase.

Since solubility of ACL-85 is likely to give chemical depolarization, low OCV and low capacities might be expected. Increasing separator thickness, and using KPF$_6$ rather than LiClO$_4$, might improve results.

26
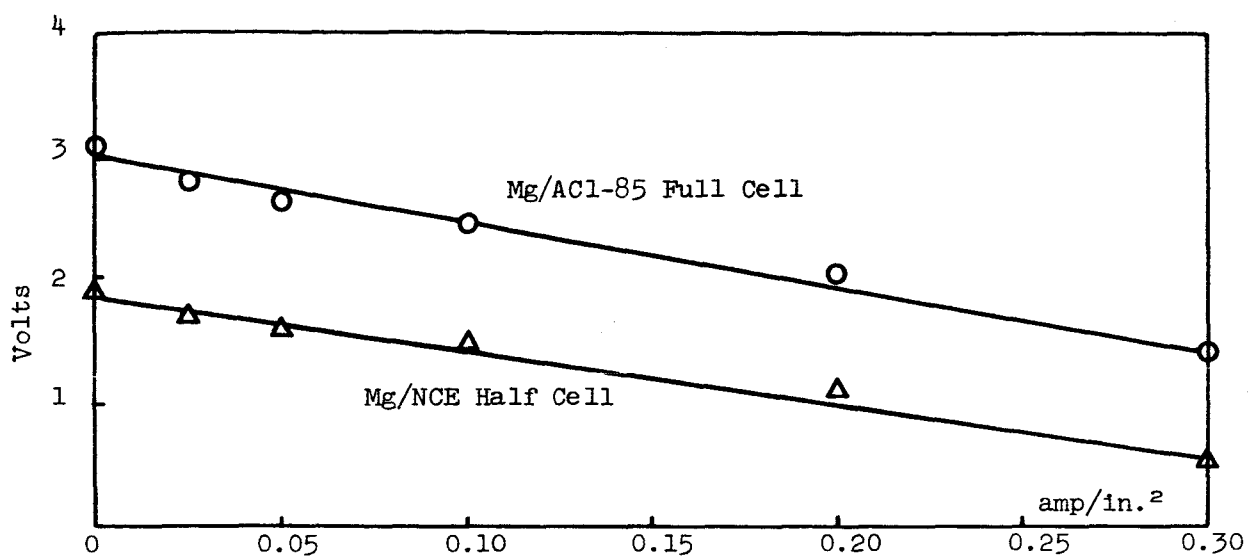
Figure 9. Current-Voltage Data on the Mg/AlCl$_3$(AN)/ACl-85 System
(A = 3 in.^{2})
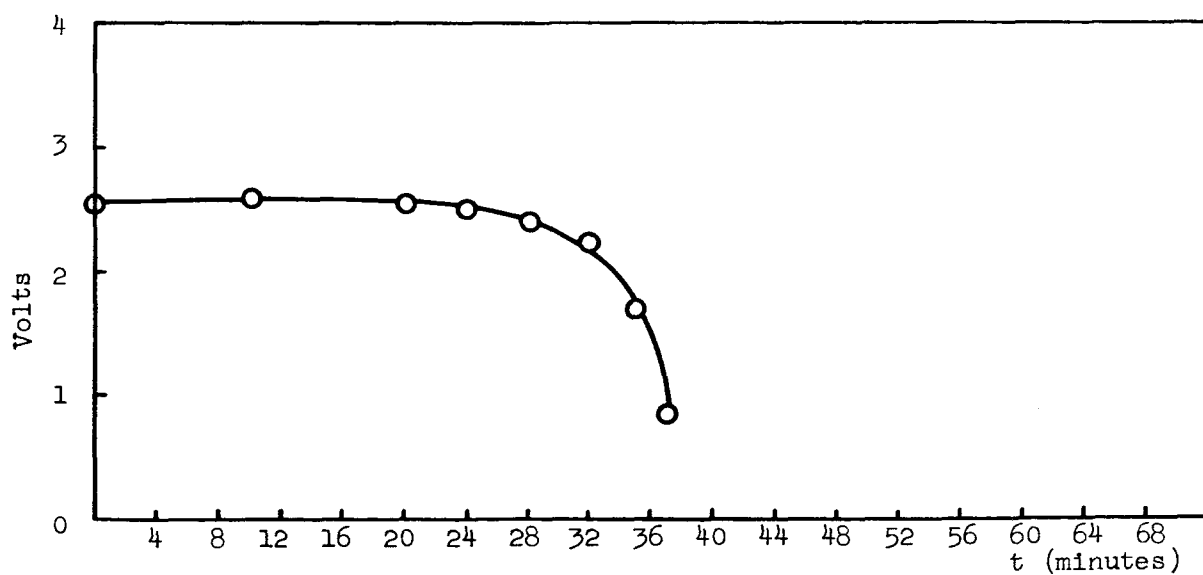
Figure 10. Constant Current Discharge of the Mg/AlCl$_3$(AN)/ACl-85
System (C.D. = 0.05 amp/in.^{2}, A = 3 in.^{2})

The results, shown in Table 14 and in Figure 11, indicate that $LiClO_4$ and KPF_6 are equally effective as electrolyte salts in methyl formate, for ACL-85 discharge. Decreasing the separator thickness also had no effect on performance with KPF_6.

In Table 14 initial ampere-minute capacities are determined by weight of the tape and iodimetric titration on a tape section. Electrochemical ampere-minute capacities are simply the products of current x minutes to reach the specified voltage or end of the experiment. Final ampere-minute capacities are determined by iodimetric titration on the used tape. "Loss" is the "Initial" capacity minus the total of the "Final" and "Electrochemical Total" capacities in amp-min.

Decreasing the current density from 0.10 amp/in.^{2} to 0.05 and 0.01 amp/in.^{2} improved voltages considerably in the $Li/KPF_6(MF)$ ACl-85 system. However, the capacities are similar at all drain rates. Thus we assume that product build-up limits the capacity or that ACl-85 discharges in steps and that the product of the two-electron discharge cannot be further reduced. Increasing the carbon percentage in the cathode was as effective as lowering the current density in increasing voltages. However, the increased electrolyte volume and electrode surface area did not improve capacities.

The "Loss" column may be a loss by chemical reaction of ACl-85 with the lithium or a loss of ACL-85 by reaction with the solvent. However, the recovery of active chlorine after dissolving ACL-85 in MF makes the reaction with solvent theory unlikely. If the loss is due to chemical depolarization, then the fact that the "loss" is no greater at 0.01 amp/in.^{2} is surprising, since the contact time is 10 times as long. The problem may be one of adsorption of products on the carbon or an inability to react the products with aqueous acidic KI solution.

The per cent utilization indicates that only one of the three chlorines are available. (Approximately the same utilization is found for the discharge of ACL-85 vs Mg in AN with $AlCl_3$--Figure 10). However, the shape of the discharge curves in methyl formate would indicate a complicated reaction mechanism. Thus the reduction may not yield the Li salt, but rather may go through a series of steps from the radical intermediate shown below.

28
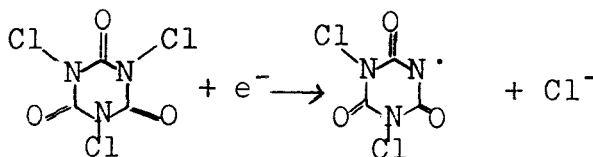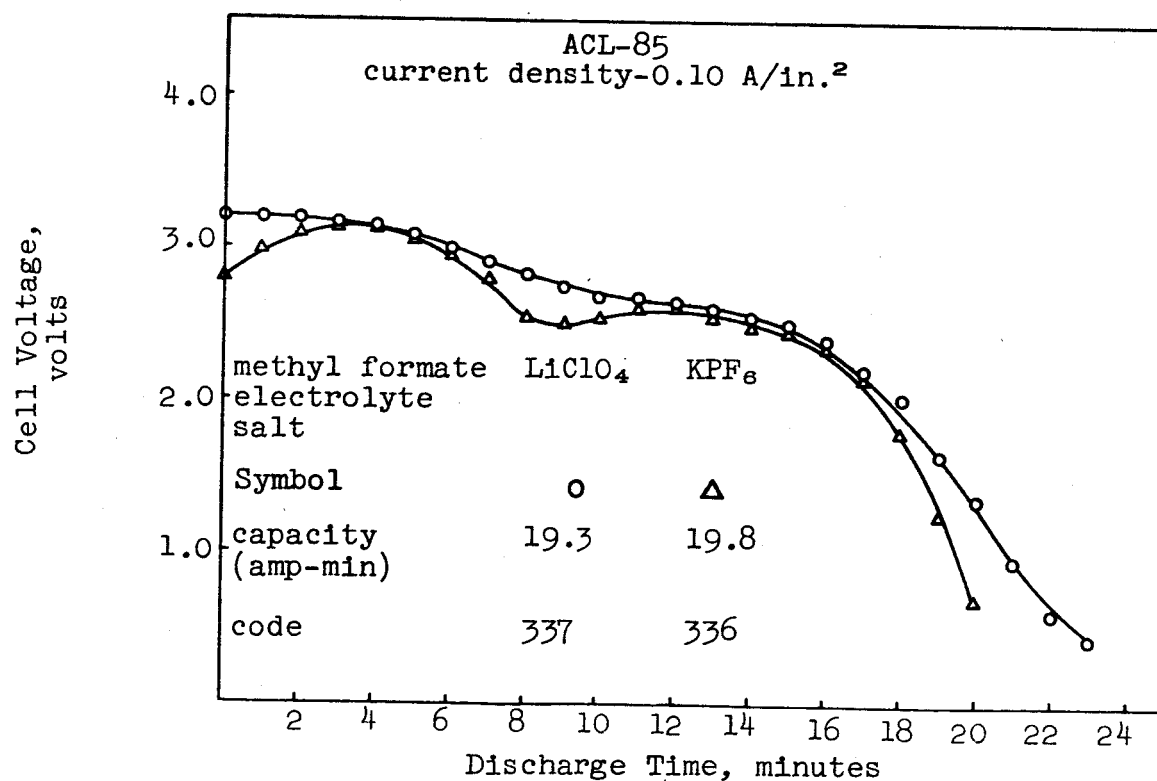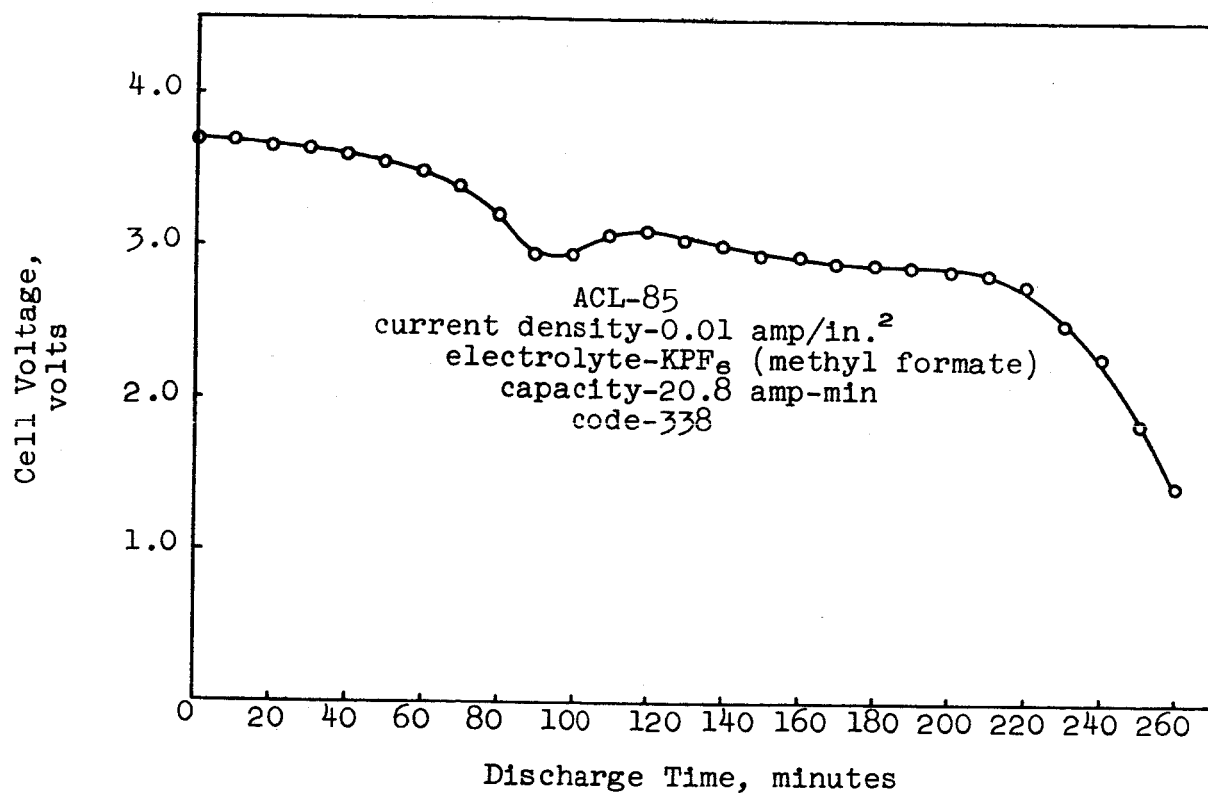
Figure 11. Discharge of the Li/ACL-85 Tape System in LiClO₄ (Methyl Formate) and KPF₆ (Methyl Formate) Electrolytes

Table 14

DISCHARGE OF Li/ACL COMPOUND TAPE CELLS IN METHYL FORMATE AT CONSTANT CURRENT

| | | | | | Capacity, amp-min. | | | | | | % Utilization at 2 volts |
| | | | | | | Electrochemical | | | | | |
Ref	Cathode	Electrolyte	Variation from Norm†	Initial	3.0v	2.5v	2.0v	Total	Final	Loss	
337	ACL-85	LiClO$_4$	-	19.3	1.8	4.5	5.4	6.9	4.0	8.4	28
308	ACL-85	LiClO$_4$	-	20.3	0	1.8	3.0	6.0	4.3	10.0	15
336	ACL-85	KPF$_6$	-	19.8	1.8(m)	4.2	5.2	6.3	4.3	9.2	26
301	ACL-85	KPF$_6$	-	23.5	0	3.6	6.6	8.7	3.2	11.6	28
306	ACL-85	KPF$_6$	1/2 sep	22.5	1.5	3.0	5.7	7.5	5.6	9.4	25
322	ACL-85	KPF$_6$	1/2 I	19.1	2.4	5.2	6.2	8.3	4.6	6.2	32
338	ACL-85	KPF$_6$	1/10 I	20.8	4.4	6.9	7.4	8.1	2.8	9.9	35
340	ACL-85	LiClO$_4$	1/2 $\frac{ACL}{SAB}$	9.8	1.2	3.3	3.6	5.1	2.4	2.3	37
341	ACL-85	KPF$_6$	1/2 $\frac{ACL}{SAB}$	10.4	0.9	2.4	3.3	3.9	2.7	3.8	32
313	ACL-59	LiClO$_4$	-	12.5	0	3.6	5.1	6.1	2.6	3.8	41
319	ACL-59	LiClO$_4$	-	8.8	0	0	3.0	4.2	3.0	1.6	34
318	ACL-59	KPF$_6$	-	8.1	0	0	0	0.3	4.5	3.3	0
329	ACL-66	LiClO$_4$	-	16.0	0	2.4	8.1	9.9	3.9	2.2	51
333	ACL-66	LiClO$_4$	-	16.1	0	2.7	6.3	8.4	5.5	2.2	39
330	ACL-66	KPF$_6$	-	14.4	0	0	0	5.4	5.7	3.3	0
335	ACL-75	LiClO$_4$	-	18.9	0.9	3.9	5.4	8.1	6.0	4.8	29
334	ACL-75	KPF$_6$	-	18.2	0	3.3(m)	7.2	9.9	6.2	2.1	40
342	ACL-70	LiClO$_4$	-	14.8	3.0	6.3	7.2	8.7	2.0	4.1	49
343	ACL-70	KPF$_6$	-	17.0	2.4(m)	3.6	6.6	11.4	1.1	4.5	39
344	ACL-70	LiClO$_4$	1/2 tape wt	7.1	0.6	1.8(m)	2.4	3.2	0.3	3.6	34
345	ACL-70	LiClO$_4$	1/2 I	16.4	6.0	7.7	8.7	9.5	0.1	6.8	53

† Norms =   I = 0.10 amp/in.²   area = 3 in.²
Separator = 0.012 in.
ACL/SAB = 2.12 g/g
Cathode wt. ≈ 0.25 g/in.²

(m)   reaches value via maximum

The resulting products could be high molecular weight species that are insoluble in the electrolyte and in the KI solution.

Other ACL compounds were tested to obtain better discharge, better chemical stability, lower solubility, and, in general, to gather information about discharge of ACL compounds and possible reduction products of ACL-85. Three compounds were available from Monsanto Company: ACL-59, ACL-66, ACL-75 and ACL-70. These materials were identified in an earlier section of this report.

ACL-59, the potassium salt of dichloroisocyanuric acid, is less soluble in organic electrolytes than ACL-85. Its stability is better than that of ACL-85 and it could be considered the first reaction product of ACL-85 in $KPF_6(MF)$ if the reaction were the simple formation of salts of the acid.

ACL-59 was reduced at 0.10 amp/in.^{2} in $LiClO_4$ (MF) but not in KPF_6 (MF). Thus we postulate that the lithium salt of dichloro-isocyanuric acid is more soluble than the potassium salt, and that this increased solubility is required for discharge at this drain rate. The discharge voltage in $LiClO_4$ is inferior to that of ACL-85 and the per cent utilization is not greatly increased. The discharge of ACL-59, -66, and -75 are shown in Figure 12.

ACL-66 is a mixed salt of two parts ACL-59 to one part ACL-85. This material, like ACL-59, would not discharge in KPF_6. The discharge in $LiClO_4$ (MF) was more efficient than with ACL-85. However, the voltage was lower.

ACL-75 discharged with KPF_6 and with $LiClO_4$ in MF. The discharge potential, however, was improved by using $LiClO_4$. The effect of Li^+ entering the solution was an increase of potential with increasing discharge time in the KPF_6 electrolyte system.

ACL-70 is dichloroisocyanuric acid. Its discharge is significantly superior to that of ACL-85 (see Figure 13). Approximately 50% utilization can be obtained above 2.0 volts at 0.10 or 0.05 amp/in.^{2}. At 0.05 amp/in.^{2}, 36% utilization is obtained above 3.0 volts. In this instance 2.0 amp-min/in.^{2} was obtained above 3.0 volts. The weight of this tape was 0.29 g/in.^{2}. Decreasing the tape weight decreased performance, similarly to that expected from increasing the current density.

3. Plans for Third Quarter (Cathode Research and Development)

The couple research phase (Task No. I) for the Mg/ACL compound system in acidic electrolyte is essentially complete. Development under Task II (Complete Cell Evaluation) will be emphasized, particularly continuous tape cell preparation and optimization of energy density output under dynamic test conditions.
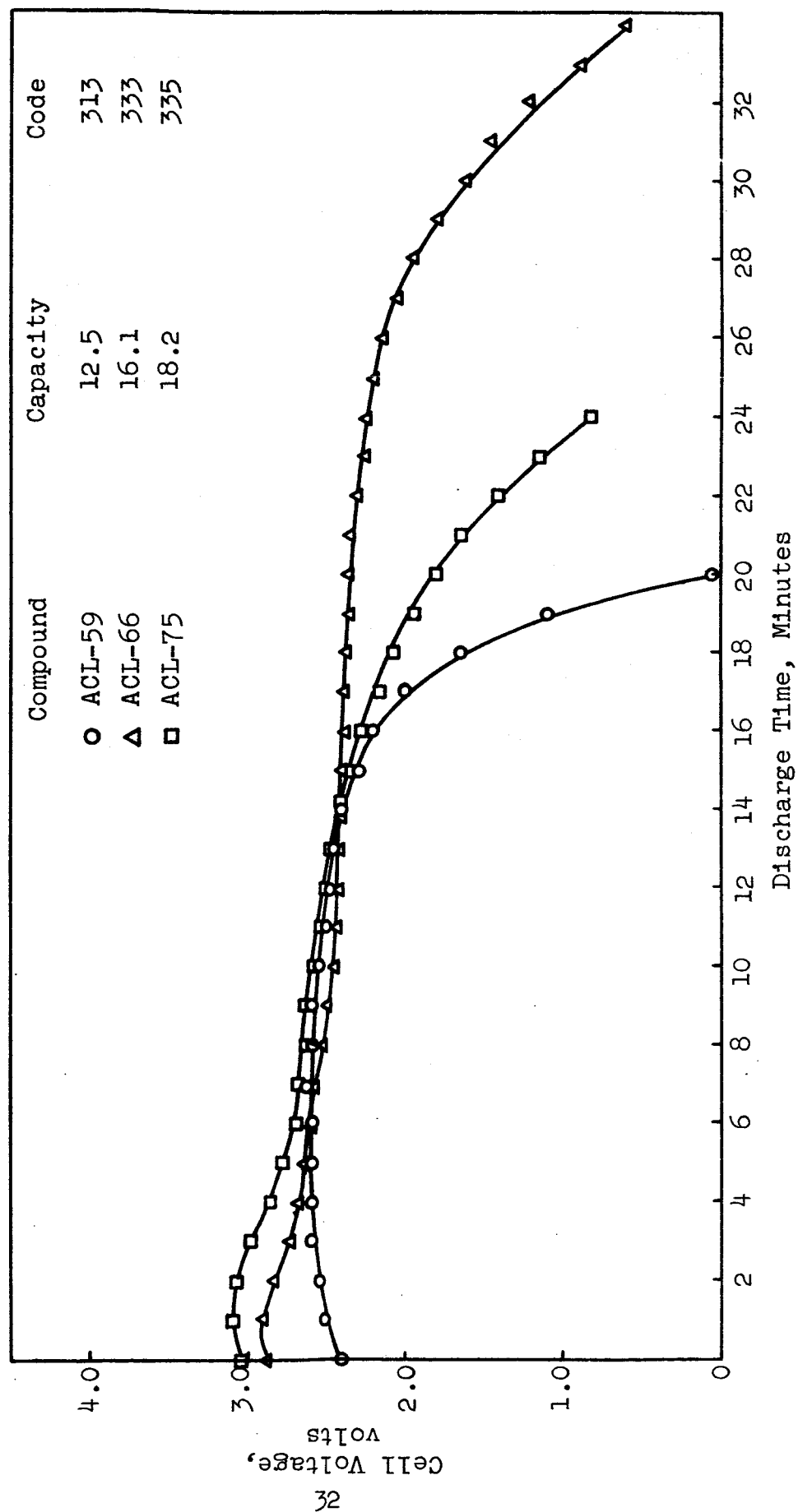
Figure 12. Discharge of ACL Compounds vs Lithium in LiClO₄(MF) at 0.10 amp/in.²

The figure is a plot of Cell Voltage, volts (y-axis, 0 to 4.0) versus Discharge Time, Minutes (x-axis, 2 to 32).

Compound	Capacity	Code
○ ACL-59	12.5	313
△ ACL-66	16.1	333
□ ACL-75	18.2	335

32
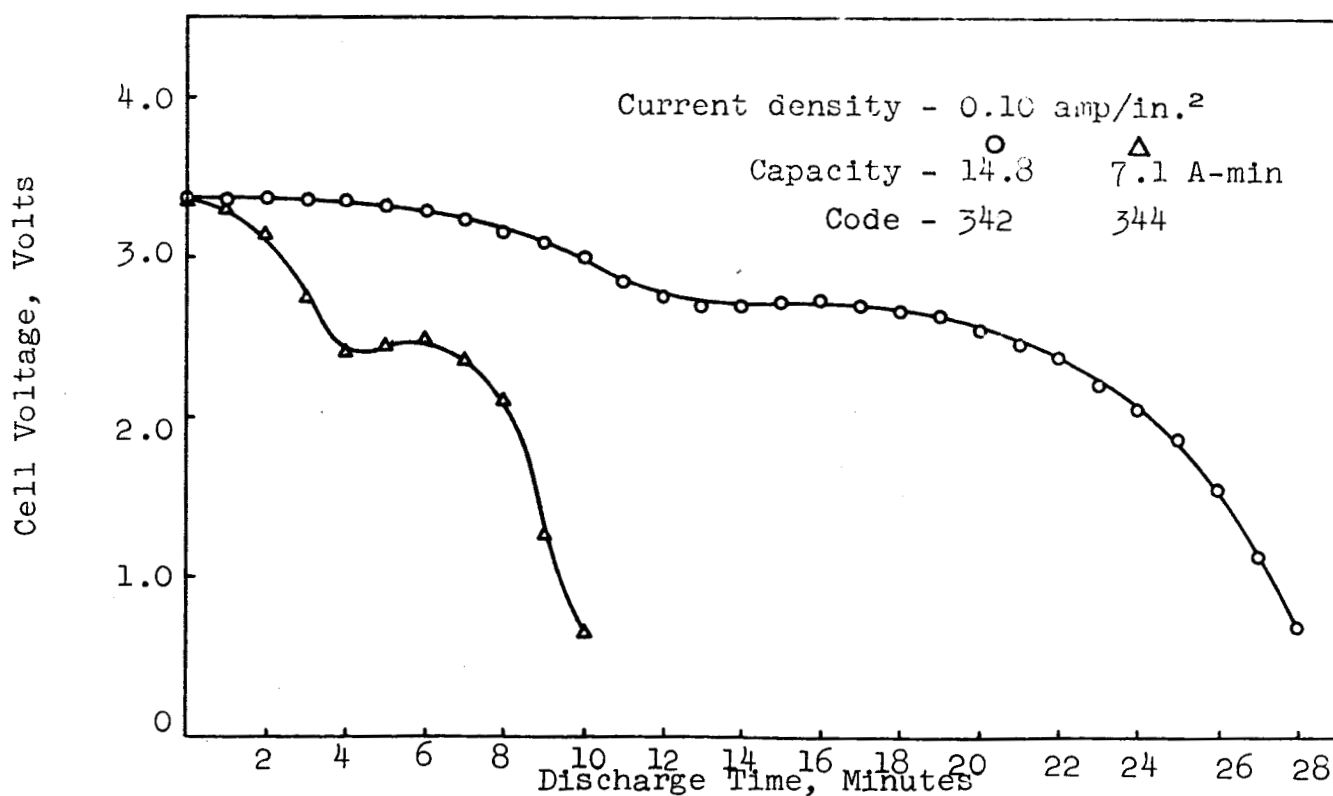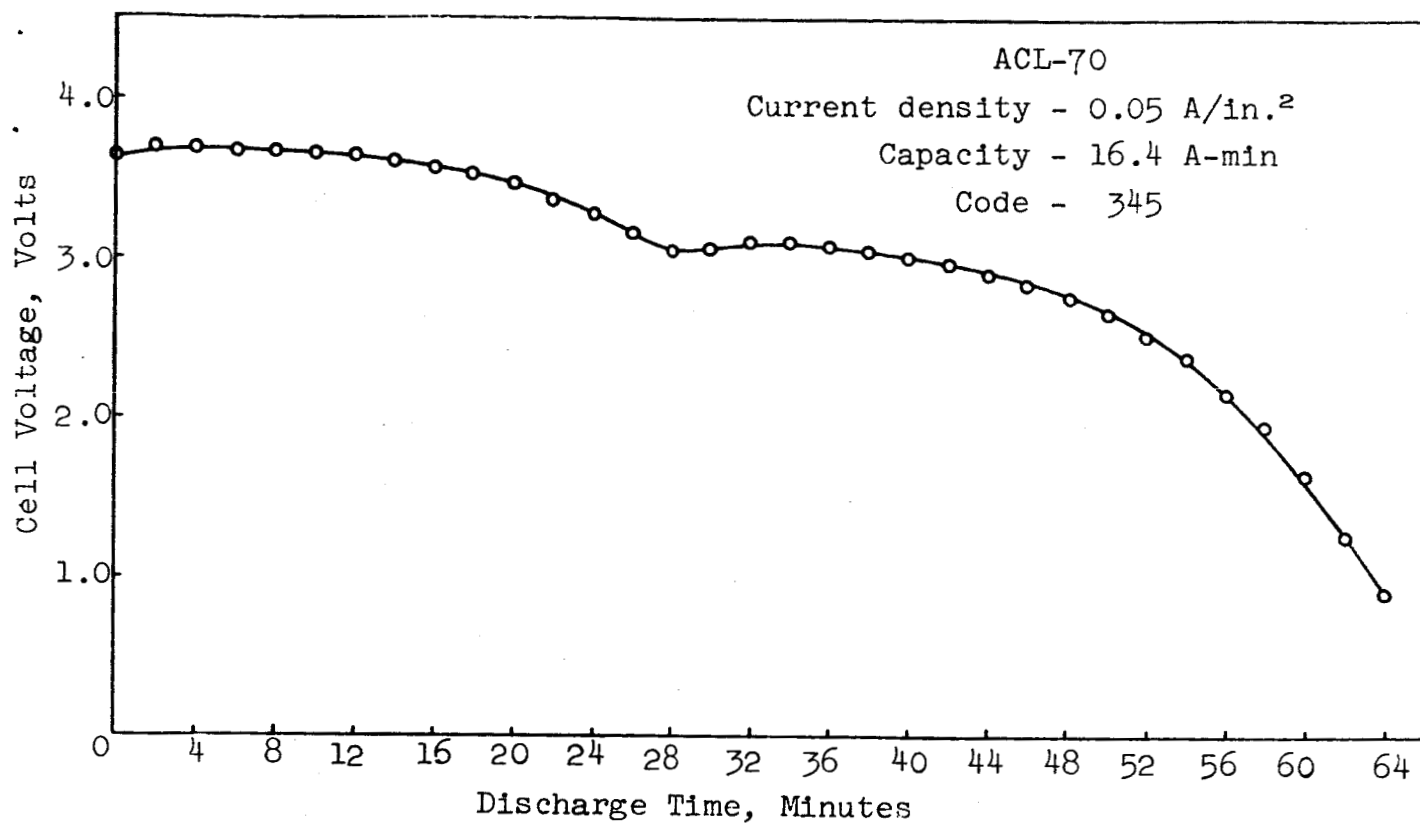
Figure 13. Discharge of the Li/ACL-70 System in LiClO$_4$ (MF)

33

A small effort will be carried out to determine the energy density limits of Mg/ACL-Compound tape cells discharged at low current densities in neutral electrolyte.

The energy density output for Li/ACL-Compound tape cells in nonaqueous electrolyte will be optimized for the static cell configuration.

CuF_2 and AgF_2 cathodes will be tested in a tape cell configuration to determine maximum current density limits.

B. ANODE RESEARCH AND DEVELOPMENT

1. Lithium in Nonaqueous Electrolyte

a. Electrode Preparation

In addition to using a solid foil electrode, two techniques for preparing a high surface area lithium anode were screened. Half cell experiments on plating lithium* on aluminum foil showed that plating from $LiClO_4$ in MF was impractical. Since LiCl is insoluble in methyl formate, electrodes were prepared from LiCl in DMF. (These could then be used in a full cell with methyl formate.) The results indicated alloy formation since the potential of lithium removal was less negative than for solid lithium. The method would have to be refined for future use.

A lithium dispersion in hexane was obtained from Foote Mineral Company, and this was spread on a separator, dried, and used as an anode for the Li/$LiClO_4$ (MF)/ACL-85 cell. The anode OCV = 1.0 volt and the cell OCV = 0 volt, indicated chemical or electrical shorting. The resistance through the anode (A = 3 in.^{2}, 1 0.05 in.) was 50 ohms, as measured between two platinum plates. Upon drying of the MF, the lithium caught fire. Since the ACL-85 was not in contact with the Li and the combustion ash showed Cl$^-$, we suspect $LiClO_4$ was the oxidant. Using KPF_6 electrolyte we again obtained a cell OCV of zero volts.

Reversing the power supply, we needed 50 ma/in.^{2} to obtain 4.0 volts, indicating a chemical discharge of this magnitude was occurring. The lithium dispersion experiments were discontinued at this point.

A lithium ribbon of 0.015 in. was obtained from Foote Mineral Company (packed in argon). This material was easier to process than the Fisher lithium, which had to be cut and pressed.

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* Technical information was received from
   P. R. Mallory on methods of plating lithium.

Without surface preparation the Foote Lithium anode was slow to reach a stable open circuit potential. Cleaning with methanol improved this situation. Cleaning with methanol and rinsing with hexane showed no further improvement. In operation in the Li/KPF$_6$ (MF)/ACL-85 cell all three anodes worked equally well under load. Thus Foote Mineral lithium ribbon with MeOH etch was used for the remainder of the quarter.

b. <u>Discharge Characteristics of Lithium Half Cells in Nonaqueous Electrolyte</u>

The screening of selected lithium-electrolyte systems in half-cells was continued, with the same electrochemical test apparatus, materials purification, and analysis as was reported last quarter. The data reported here (Table 15) are presented in a manner similar to Table 6 of Report No. 1. These data complete our lithium anode half-cell program.

The test apparatus will be used to improve full cells by controlling and studying variables in the half-cell tests or to test new electrolyte systems if any are found that warrant half-cell investigation.

The data collected in this phase have been based on systems largely suggested by other researchers in the nonaqueous battery field. However, the data were collected to determine applicability to dry tape use, where lithium stability is less important than current drain.

Methyl formate was previously shown to be a good electrolyte for lithium anodes. However, its low boiling point (31°C) is undesirable for certain practical applications. Hence ethyl-formate (bp 54°C) was tested and compared with other likely electrolyte systems. The conductivity of LiClO$_4$ in ethyl formate (0.64 x 10^{-2} ohm^{-1}cm^{-1}) is only half that of the methyl formate system, whereas the conductivity with KPF$_6$ is only 7 x 10^{-4} ohm^{-1}cm^{-1}. The latter system was therefore not tested with lithium. The results indicate that LiClO$_4$ (ethyl formate) system might be useful for some applications.

Since there had been an indication that water improved the discharge of ACL compounds in methyl formate, the effect of water on lithium performance was studied in this electrolyte. Methyl formate/water samples from 0.065 mg H$_2$O/ml to 10 mg/ml were prepared and the current-voltage results showed no decreased performance. At increased water concentrations gassing increased and performance improved slightly, due to improved conductivity.

It had been observed while cleaning lithium with methanol that the gassing of lithium decreased with time. We prepared a 1.4M solution of lithium methoxide (LiOMe) in methanol and found

Table 15

LITHIUM ANODE (FREE ELECTROLYTE) HALF CELL DATA

Electrolyte System	$K \times 10^2$	H_2O mg/ml	Gassing	Voltages (-ve vs NCE) at Various Current Densities (amps/in²)								IR at Volts	I A/in²	Notes
				0	0.025	0.05	0.1	0.2	0.3	0.4	0.5			
Ethylformate-LiClO₄(1M)	0.64	2.1	none	3.0	2.9	2.8	2.65	2.35	2.05	1.75	1.45	0.60	0.2	No change noticed
Methylformate-NaSbF₆(0.27M)	0.52	0.10	none	3.15	2.80	2.65	2.5	2.3	2.1	2.0	1.9	not square		Grey coat on surface
Methylformate-MPF₆(0.55M)	0.72	0.3	yes	2.95	2.9	2.85	2.7	2.45	2.20	1.95	1.65	0.65	0.2	Solution turns yellow
γ-Butyrolactone-MPF₆(1M)	1.36	0.74	yes	3.05	3.0	3.0	2.95	2.75	2.45	fails		0.22	0.2	Loose grey film on surface
Dimethylformamide-NaSbF₆(0.25M)	1.2	0.26	slight	3.20	3.00	2.85	2.65	2.40	2.05	fails		0.40	0.2	Grey-black surface
Methanol-LiOMe(1.4M)	1.06	-	yes	2.60	-0.20									
Dimethylsulfoxide-LiCl(1M)	0.67	0.85	none	3.05	2.85	2.25	2.60	2.05	fails			0.7	0.2	Film formed
Methyl Formate-LiClO₄(1M)	1.22	0.065		3.0	2.95	2.90	2.80	2.60	2.40	2.25	2.15	0.5	0.2	
		2.0		3.0	2.95	2.90	2.80	2.60	2.45	2.30	2.20	0.5	0.2	
		3.0		3.0	2.95	2.90	2.85	2.75	2.65	2.60	2.50	0.25	0.2	
		5.0		2.95	2.95	2.90	2.80	2.70	2.55	2.40	2.20	0.3	0.2	
		7.0		3.00	2.95	2.95	2.90	2.80	2.70	2.60	2.45	0.2	0.2	
		10.0		3.00	3.0	2.95	2.90	2.80	2.70	2.55	2.40	Gas Interference		

the conductivity of the solution to be 1.06×10^{-2} ohm^{-1}cm^{-1}. However, when lithium was tested as a half cell with this electrolyte, the lithium developed a passive coating and was ineffective as an anode.

A dry, purified sample of dimethylsulfoxide (DMSO) was made available to us from another group in our laboratory. This solvent was tested with Li and Mg to obtain a comparison to data from the first quarter's work. The conductivity of the 1M solution of LiCl was 0.67×10^{-2} ohm^{-1} cm^{-1}.

The other results presented in Table 15 are self explanatory; the systems were chosen to complete our screening program.

An $AlCl_3$(AN) electrolyte was prepared and was found to be too reactive for testing with lithium.

2. Magnesium in Nonaqueous Electrolyte

The experiments described in this section were performed with the same materials and equipment as for the lithium studies. In many instances the same solutions were used. Last quarter the importance of magnesium cleaning was emphasized. During this report period other etch solutions were tried. The one chosen for use is the following:

> 35 ml methanol
>
> 35 ml ethanol (absolute)
>
> 5 ml Ansul 141 Ether
>
> 6 g HCl (gas)
>
> 10 ml HNO$_3$ (98%)

This etch solution is based on patent literature (ref. 3), but it is more nearly nonaqueous than the patent etch. The etch solutions were evaluated on the LiCl (γ-butyrolactone) system. This etch solution was used for all the tests with magnesium reported in this report.

Several methanolic electrolytes were tested with magnesium to attempt to improve the voltage from that in the aqueous system. Anode gassing would also be expected to be less in methanol. The results are shown in Table 16. The oscilloscope trace of each of these tests was a square wave, indicating that, at the current density tested (0.2 amp/in.^{2}), the polarization was entirely due to IR loss.

In acidic electrolytes gassing was heavy and potentials were lower than in neutral or basic solutions. Acidic methanol solutions appear to offer no advantages over the aqueous electrolytes now in use in this program. In basic solution, voltages

Table 16

MAGNESIUM-NONAQUEOUS ELECTROLYTE SYSTEMS

Electrolyte System	K ohm^{-1}cm^{-1} x 10^2	Gassing	Voltage vs NCE at Various Current Densities (amp/in.$^{-2}$)								IR at I 1A/in.^{2}	
			0.00	0.025	0.05	0.10	0.20	0.30	0.40	0.50	volts	A/in.^{2}
Methanol-HCl (gas)(0.1M)	1.8	v. heavy	1.93	1.89	1.87	1.80	1.65	1.51	1.32	1.19	0.35	0.2
Methanol-AlCl$_3$ (0.5M)	0.84	heavy	1.94	1.90	1.83	1.73	1.52	1.29	1.07	0.82	0.55	0.2
Methanol-LiAlCl$_4$ + AlCl$_3$ (0.75M + 0.05M)	1.42	moderate	1.98	1.93	1.87	1.76	1.58	1.37	1.14	0.87		
Methanol-LiCl (1M)	1.8	light	2.05	1.98	1.92	1.80	1.59	1.40	1.22	1.08	0.60	0.3
Methanol-LiClO$_4$ (1M)	3.1	light	2.10	2.02	1.98	1.89	1.73	1.60	1.44	1.30	0.45	0.3
Methanol-LiOMe (1.4M)	1.06	slight	2.20	2.10	2.00	1.80	1.65	1.20			0.40	0.2
Ethylformate-LiClO$_4$ (1M)	0.64	none	1.72	0.96	0.50	0.15					not square	
Methylformate-MPF$_6$*	0.72	none	1.73	0.94	0.49						not square	
γ-BL*-MPF$_6$* (1M)	1.36	none	1.63	0.91	0.65						not square	
DMF*-NaSbF$_6$(0.25M)	1.2	none	1.51	1.0	0.87	0.64					not square	
AN*-AlCl$_3$ (1M)	2.5	none	1.86	1.75	1.61	1.49	1.42	1.30	1.06	0.80	not square	
DMSO*-LiCl (1M)	0.67	none	1.5	1.5	1.47	1.25	fails				not square	

γ-BL = γ-butyrolactone; DMF = dimethylformamide; AN = acetonitrile ; DMSO = dimethylsulfoxide

MPF$_6$ = morpholinium hexafluorophosphate

improve significantly. Full cell tests have been performed with the LiOMe(MeOH) system.

Even with the present etch solution used in the dry box, other nonaqueous (non-protonic) systems showed poor performance in general. Again this quarter, the slight beneficial effect of chloride ion can be seen in breaking down the passive layer. Magnesium, with these non-protonic solvents, showed a minimum voltage in the oscilloscope trace, indicating a breakdown of the passive film with continuing electrolysis (Quarterly Report No. 1).

The $AlCl_3$ in the $AlCl_3$ acetonetrile system developed by Globe Union (ref. 16) is apparently capable of breaking down the passive film on magnesium to an extent where the anode operates effectively. This system was tested in half cell, and in full cell with ACl-compounds (see Section A2b).

In the half cell test of $Mg/AlCl_3$, $1\underline{M}$ in acetonitrile K = 2.55×10^{-2} ohm^{-1} cm^{-1}) a slight gassing and passivation of the magnesium was noticed at open circuit (peak in oscilloscope trace). The magnesium also improved with use.

3. <u>Plans for Third Quarter (Anode Research and Development)</u>

Lithium will continue to be used as the major nonaqueous system anode in conjunction with full cell testing of various cathodes. The foil configuration operates satisfactorily, and further anode testing will be directed to evaluating new tape anode configurations.

Thin-foil beryllium anode material, suitable for a tape configuration, will be tested in strong basic aqueous electrolyte.

III. TASK II - TAPE CELL EVALUATION

A. TAPE CELL PREPARATION

Full scale production of continuous lengths of Mg/ACL-85 tapes, scheduled for the second quarter, was postponed to complete the analysis of ACL-85 instability. A new binder system must be devised for ACL-compound tapes. Production of tape lengths suitable for dynamic testing is expected by the middle of the third quarter.

B. DYNAMIC TESTING

Complete evaluation of the Mg/ACL-85 system and other Mg/ACL-compound systems will be carried out during the third quarter. Energy density output will be optimized under these test conditions.

IV. SUPPORTING RESEARCH: TEST EQUIPMENT DESIGN AND IMPROVEMENT

No work was required during the second quarter.

A suitable modification of the present dynamic test facility will be designed to evaluate lithium anode based nonaqueous tape systems during the third quarter.

V. REFERENCES

1. Kirk-Othmer, "Encylopedia of Chemical Technology", Vol. 4, second edition. Interscience, N. Y. 1964, 924.

2. Ibid., Vol. 5, 15.

3. W. F. Meyers and S. G. Abends, "Development of High Energy Density Primary Batteries 200 Watt Hours per Pound Total Battery Weight Minimum", Contract NAS3-6004, Quarterly Report No. NASA CR-54659.

4. B. A Gruber, et al. "Feasibility Proof of Dry Tape", Contract NAS3-2777, Final Report, 31 March 1964.

5. A. H. Wisken, U. S. Patent 2,849,297.

6. W. E. Elliott et al.,"A Program to Develop A High-Energy Density Primary Battery with A Minimum of 200 Watt Hours Per Pound of Total Battery Weight", Contract NAS3-6015, NASA CR-54450, August 1965.

Table A-1

STATIC CELL DISCHARGE DATA FOR TRI-N-CHLOROTRIAZINETRIONE ("ACL-85®") TAPE CATHODES

Cathode Composition: Tri-N-chlorotriazinetrione (Monsanto ACL-85)
Acetylene Black (Shawinigan)--unless otherwise noted
Binder (2.75 wt. %)--polyvinyl formal--unless otherwise noted
Fibrous filler--1/8 in. dynel or carbon fiber

Tape Cell Area: 3 inches x 1 inch
Anode: Primary magnesium (Dow)
Separator: 4 mil dynel unless otherwise noted

Run No.	Wt.% Active Material	Theoretical Capacity amp-min/in²	Electrolyte	Current Density amp/in.²	Cathode Efficiency %	Operating Voltage, volts	Remarks
80401-2	65	9.5	2M AlCl₃·0.5M HCl	0.50	39	2.4	
80401-3	65	9.5	"	"	35	2.4	
80401-8	65	10	"	"	44	2.3	Nylon separator
80401-9	65	8.8	"	"	39	2.4	Polypropylene separator
80403-1	65	8.7	2M AlCl₃·1M HCl	"	48	2.45	"
80403-2	65	9.3	0.5M HCl	"	59	2.50	Acetylene black vacuum dried for 24 hours at 200°C
80403-3	65	9.2	"	0.67	52	2.15	"
80403-5	65	8.7	1M HCl	0.33	51	2.45	"
80403-6	65	9.6	0.5M HCl	0.50	62	2.45	
80404-1	65	7.8	"	"	61	2.30	
80404-5	65	8.5	"	"	53	2.35	
80405-1	65	8.5	"	"	48	2.4	Polypropylene separator
80405-5	65	10.3	"	"	50	2.45	Nylon separator
80404-2	65	8.5	1M HCl	0.67	44	2.40	
80404-3	65	10.1	"	0.50	50	2.00	
80404-4	65	10.1	0.5M HCl	0.33	50	2.35	
80404-6	65	8.5	"	0.50	42	2.30	Acetylene black vacuum dried for 20 hours at 200°C
80407-1	70	8.9	"	0.67	54	2.40	"
80407-2	70	11.4	1M HCl	0.33	51	2.20	"
80407-3	70	9.0	0.5M HCl	0.50	44	2.05	30 hours at 185°C
80408-1	65	10.5	"	0.67	50	2.30	"
80408-2	65	8.9	1M HCl	0.33	50	2.35	
80408-3	65	8.9	"	0.50	59	2.05	
80408-4	65	8.1	"	0.33	55	2.45	
80408-5	65	8.9	1M HCl	0.50	54	2.35	
80408-6	65	8.1	"	0.67	51	2.45	
80410-1	65	8.1	0.5M HCl	0.50	50	2.15	
80412-3	50	6.7	0.5M HCl	0.67	34	2.05	
80412-4	50	7.0	"	0.50	54	1.85	
80412-5	50	6.6	"	"	45	2.10	
80414-1	65	11	"	0.50	57	2.20	
80414-2	65	10.7	"	0.67	54	2.35	Polypropylene separator-Acetylene black preground
80415-1	65	10	"	0.50	56	2.25	Polypropylene separator-poor wetting

Table A-1 (continued)

Run No.	Wt.% Active Material	Theoretical Capacity amp-min/in.²	Electrolyte	Current Density amp/in.²	Cathode Efficiency %	Operating Voltage, volts	Remarks
80415-2	65	13	2M AlCl₃·0.5M HCl	0.67	57	2.20	
80414-4	65	12.1	" 1M HCl	0.50	48	2.45	
80414-5	65	12.2	" 0.5M HCl	0.67	49	2.30	9.7% active chlorine analysis after discharge
80415-3	65	13.3	" 1M HCl	0.50	49	2.35	4.1% active chlorine analysis after discharge
80418-1	65	7	2M AlCl₃·0.5M HCl	0.50	56	2.15	5% active chlorine analysis after discharge
80418-2	65	11.5	" 1M HCl	0.67	54	2.20	
80418-3	65	3.4	"	0.33	56	1.65	
80418-9	65	9.8	2M LiClO₄	0.17	44	1.75	
80418-10	65	16.1	"	0.50	62	2.20	
80421-1	65	8.3	1.5M AlCl₃·0.7M HCl ·0.5M LiClO₄ 1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.17	74	2.55	
80421-3	65	11.0	2M AlCl₃·1M HCl	0.67	46	2.20	
80421-4	65	9.6	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.50	64	2.30	
80421-6	65	7.2	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.50	69	2.35	
80423-1	65	4.0	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.17	72	2.50	
80423-2	65	4.0	2M AlCl₃·1M HCl	0.33	53	2.50	
80423-3	65	8.1	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	72	2.30	
80423-4	65	6.5	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.33	68	2.30	
80423-5	65	6.9	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	66	2.40	
80423-7	65	5.8	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.33	68	2.40	
80423-9	65	6.5	2M AlCl₃·0.5M HCl	0.33	50	2.40	
80423-10	65	4.3	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.33	58	2.20	
80426-1	60	3.4	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.17	75	2.40	
80426-2	60	6.8	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.50	64	2.30	
80426-3	60	7.4	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	69	2.35	
80426-4	60	5.5	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.50	74	2.25	
80426-7	60	5.3	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.50	49	2.30	
80426-9	60	3.3	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.17	69	2.30	
80429-1	70	6.2	2M AlCl₃·1M HCl	0.50	57	2.25	
80429-2	70	6.1	2M AlCl₃·0.5M HCl	0.50	66	2.20	
80429-3	70	7.4	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	55	2.10	
80429-4	70	6.2	2M LiClO₄	0.50	did not maintain 2.00 volts		
80429-8	70	4.6	1M AlCl₃·1M LiClO₄ ·0.5M HCl	0.50	bb	2.10	

Table A-1 (continued)

Run No.	Wt.% Active Material	Theoretical Capacity, amp-min/in.^{2}	Electrolyte	Current Density, amp/in.^{2}	Cathode Efficiency %	Operating Voltage, volts	Remarks
80429-9	70	5.6	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	63	2.10	
80429-10	70	7.6	1M AlCl₃·1M LiClO₄·1M HCl	0.67	38	2.00	
80431-1	67.5	4.9	2M AlCl₃·0.5M HCl	0.50	57	2.25	
80431-2	67.5	4.4	1M AlCl₃·1M LiClO₄·0.5M HCl	0.50	58	2.10	
80431-3	67.5	6.0	2M AlCl₃·1M HCl	0.50	44	2.30	
80431-4	67.5	4.9	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	58	2.25	
80431-5	67.5	5.4	1M AlCl₃·1M LiClO₄·0.5M HCl	0.50	61	2.15	
80431-6	67.5	5.8	1.5M AlCl₃·0.5M LiClO₄·0.5M HCl	0.50	65	2.25	
80431-7	67.5	5.4	1.5M AlCl₃·0.5M LiClO₄·0.6M HCl	0.50	55	2.20	
80436-1	65	5.6	1M AlCl₃·1M LiClO₄·0.3M HCl	0.50	63	2.10	Tested immediately after drying
80436-2	65	6.6	2M AlCl₃·0.5M HCl	0.50	44	2.35	Tested after 24 hours in desiccator
80436-3	65	5.3	1M AlCl₃·1M LiClO₄·0.3M HCl	0.50	68	2.25	Tested after 24 hours in desiccator
80436-7	65	5.3	2M AlCl₃·0.5M HCl	0.50	42	2.35	Tested after 24 hours standing in air
80436-10	65	8.7	1M AlCl₃·1M LiClO₄·0.3M HCl	0.50	57	2.10	Tested after 24 hours standing in air
80439-1	65	4.2	2M LiClO₄	0.50	28	1.72	
80439-2	65	4.8	2M AlCl₃	0.50	72	2.20	
80439-3	65	5.9	1.5M AlCl₃·0.5M LiClO₄	0.50	75	2.20	
80439-4	65	6.2	1.5M LiClO₄·0.5M AlCl₃	0.50	35	1.90	
80439-5	65	5.9	1M AlCl₃·1M LiClO₄	0.50	55	1.95	
80439-6	65	4.1	1.5M AlCl₃·0.5M LiClO₄	0.50	63	2.00	4 cc electrolyte used (Added by pipet)
80439-8	65	4.1	1.5M AlCl₃·0.9M LiClO₄	0.50	54	2.00	2 cc electrolyte used
80439-9	65	4.5	1.1M AlCl₃·0.5M LiClO₄	0.50	70	2.15	excess electrolyte used
80439-10	65	8.0	1.5M AlCl₃·0.5M LiClO₄	0.50	72	2.15	7 cc electrolyte used
80442-1	65	4.6	1.5M AlCl₃·0.5M LiClO₄	0.50	59	2.10	5 cc electrolyte
80442-2	65	4.3	1.5M AlCl₃·0.5M LiClO₄	0.50	71	2.10	6 cc electrolyte
80442-4	65	3.4	1M AlCl₃·1M MgCl₂	0.50	67	2.15	6 cc electrolyte
80442-5	65	4.3	2M AlCl₃	0.50	67	2.15	10 cc electrolyte
80442-6	65	9.6	2M AlCl₃·0.5M HCl	0.50	63	2.40	excess electrolyte
80442-7	65	4.6	2M AlCl₃·0.1M HCl	0.50	51	2.30	excess electrolyte
80442-8	65	5.4	1.5M AlCl₃·0.5M LiClO₄	0.50	72	2.10	8 cc electrolyte
80442-9	65	6.7	1.5M AlCl₃·0.5M LiClO₄	0.50	76	2.20	10 cc electrolyte

Table A-1 (continued)

Run No.	Wt.% Active Material	Theoretical Capacity amp-min/in.²	Electrolyte	Current Density amp/in.²	Cathode Efficiency %	Operating Voltage, volts	Remarks
80442-10	65	3.9	1.5M AlCl₃·0.5M MgCl₂	0.50	69	2.25	12 cc electrolyte
80445-1	65	6.9	1.5M AlCl₃·0.5M MgCl₂	0.50	80	2.20	8 cc electrolyte--tested immediately after drying
80445-2	65	7.1	1.5M AlCl₃·0.5M MgCl₂	0.50	83	2.10	9 cc electrolyte--tested after 24 hours under vacuum
80445-3	65	7.6	1.5M AlCl₃·0.5M MgCl₂	0.50	75	2.15	4 cc electrolyte
80445-4	65	6.7	1M AlCl₃·1M MgCl₂	0.50	76	2.10	6 cc electrolyte
80445-5	65	6.1	1.5M MgCl₂·0.5M AlCl₃	0.50	42	1.90	8 cc electrolyte
80445-6	65	6.9	2M AlCl₃	0.50	73	2.20	6 cc electrolyte
80445-7	65	4.7	1.8M AlCl₃·0.2M MgCl₂	0.50	76	2.15	
80445-8	65	6.1	2M MgCl₂	0.50	31	1.80	
80445-9	65	8.6	2M AlCl₃·0.5M HCl	0.50	58	2.30	
80445-10	65	10.0	pH-4 buffer--CH₃COOH,CH₃COONa	0.50	Ran for a few minutes between 2.00 and 1.50 volts		
80450-1	65	7.4	1.5M AlCl₃·0.5M MgCl₂	0.50	81	2.30	
80450-2	65	8.2	1.3M AlCl₃·0.7M MgCl₂	0.50	77	2.20	
80450-3	65	7.4	2M AlCl₃	0.50	79	2.35	Tested after 84 hours air storage
80450-4	65	6.1	1M AlCl₃·1M MgCl₂	0.50	84	2.20	Tested after 84 hours air storage
80450-5	65	7.4	1.3M MgCl₂·0.7M AlCl₃	0.50	65	2.00	
80450-6	65	5.1	1M AlCl₃·1M MgCl₂	0.67	78	1.90	
80450-7	65	6.2	1.5M AlCl₃·0.5M MgCl₂	0.67	80	2.20	
80450-8	65	5.0	2M MgCl₂	0.17	54	1.80	
80450-9	65	8.0	2M AlCl₃·1M HCl	0.50	60	2.35	
80450-10	65	8.4	2M AlCl₃·0.5M HCl	0.50	65	2.35	
80455-1	65	11.9	2M MgCl₂	0.05	59	2.10	
80455-10	65	19.7	2M AlCl₃·0.5M HCl	0.83	56	2.30	
80455-11	65	20.6	1.5M AlCl₃·0.5M MgCl₂	0.83	82	2.10	
80455-12	65	18.3	1.5M AlCl₃·0.5M MgCl₂	0.83	74	2.10	
80455-13	65	21.3	1.5M AlCl₃·0.5M MgCl₂	1.0 / 0.5	71 / 72	1.45 / 2.30	
80455-14	65	20	1.5M AlCl₃·0.5M MgCl₂	0.67	76	2.30	
80455-15	65	19.5	1.5M AlCl₃·0.5M MgCl₂	0.67	76	2.30	8 cc electrolyte used
80455-16	65	19.7	2M AlCl₃·0.5M HCl	0.50	71	2.50	
80455-17	65	22.1	1.3M AlCl₃·0.7M MgCl₂	0.67	77	2.10	
80455-18	65	23.9	1M AlCl₃·1M MgCl₂·0.25M HCl	0.50	73	2.25	

Table A-1 (continued)

Run No.	Wt.% Active Material	Theoretical Capacity, amp-min/in.²	Electrolyte	Current Density, amp/in.²	Cathode Efficiency %	Operating Voltage, volts	Remarks
80455-19	65	22.2	1M AlCl₃·1M MgCl₂	0.67	54	2.00	8 cc electrolyte used
80455-20	65	26	1.5M AlCl₃·0.5M MgCl₂	1.00	67	2.00	
80460-1	70	17.5	2M AlCl₃·0.5M HCl MgCl₂	0.67	55	2.15	
80460-3	70	19	1.5M AlCl₃·0.5M MgCl₂	0.67	71	2.10	
80477-1	65	4.7	2M MgCl₂	0.17	50	1.95	
80477-2	65	5.6	2M AlCl₃·0.5M HCl	0.50	60	2.25	
80477-3	65	5.9	2M Mg(ClO₄)₂	0.17	43	1.90	
80477-4	65	10.8	1.5M AlCl₃·0.5M MgCl₂	0.50	75	2.10	
80477-5	65	14.8	2M AlCl₃	0.67	83	2.20	
80477-6	65	10.0	2M MgBr₂	0.17	63	1.90	
80477-7	65	10.0	2M AlCl₃·0.5M HCl	1.00	46	1.80	
80477-8	65	11.7	1.5M AlCl₃·0.5M MgCl₂	0.50	61	2.15	
80477-9	65	11.2	2M AlCl₃	0.67	53	2.05	
80477-12	65	14.3	1.5M AlCl₃·0.5M MgCl₂	1.00	48	1.60	
80482-1	65	9.8	2M AlCl₃	0.50	68	2.35	No binder (PVF)
80482-5	65	11.7	1.5M AlCl₃·0.5M MgCl₂	0.67	67	2.20	No binder (PVF)
80482-6	65	8.8	2M AlCl₃·0.5M HCl	0.67	56	2.20	No binder (PVF)
80482-2	65	10.3	2M AlCl₃·0.5M HCl	0.50	79	2.40	No binder (PVF)
80482-3	65	14.8	1.3M AlCl₃·0.7M MgCl₂	0.50	75	2.20	No binder (PVF)
80482-4	65	12.2	2M AlCl₃·0.5M HCl MgCl₂	0.67	50	2.10	No binder (PVF)
80482-7	65	7.4	2M MgCl₂	0.17	75	2.00	No binder (PVF)
80482-10	65	4.7	2M MgBr₂	0.05	68	2.10	No binder (PVF)
80482-11	65	7.2	1.3M AlCl₃·0.7M MgCl₂	0.33	75	2.45	No binder (PVF)

Table A-2

STATIC CELL DISCHARGE DATA FOR ACL COMPOUND TAPE CATHODES

Cathode Formulation: Identical to that for ACL-85 in Table A-1
Anode: Primary Magnesium (Dow)
Cell Area: 3 inches by 1 inch

Run No.	Active Material	Wt.% Active Material	Theoretical Capacity amp-min/in.^{2}	Electrolyte	Current Density amp/in.^{2}	Cathode Efficiency %	Operating Voltages volts	Remarks
80466-1	ACL-59	65	4.3	2M AlCl$_3$	0.50	fell below	1.5 volts after 2 minutes	
80466-2	"	"	7.1	2M MgCl$_2$	"	fell below	1.0 volt immediately	
80466-4	"	"	8.7	2M AlCl$_3$·0.5M HCl	"	46	2.10 Sharp dip to 1.6 v initially	
80466-6	"	"		CH$_3$COOH,CH$_3$COONa buffer	"	fell below	1.0 volt immediately	
80466-7	"	"	10.1	1.5M AlCl$_3$·0.5M MgCl$_2$	"	53	2.10	
80466-10	"	"	10.2	"	"	51	2.15	
80483-1	ACL-75	"	5.8	"	"	71	2.15	
80483-2	"	"	8.6	2M AlCl$_3$·0.5M HCl	"	47	2.05	
80483-9	"	"	6.2	2M MgBr$_2$	"	75	2.20	
80483-10	"	"	6.6	2M MgCl$_2$	0.05	77	1.90	
80484-2	ACL-66	"	8.2	"	0.17	50	1.90	
80484-7	"	"	6.8	1.5M AlCl$_3$·0.5M MgCl$_2$	0.50	25	1.75	
80484-11	"	"	8.2	"	"	56	2.10	
80486-1	"	"	7.1	2M MgBr$_2$	0.05	75	2.15	No binder
80486-2	"	"	8.8	1.5M MgCl$_2$·0.5M AlCl$_3$	0.33	70	2.00	"
80486-3	"	"	9.0	2M MgBr$_2$	0.05	60	2.05	"
80486-4	"	"	4.0	1.5M AlCl$_3$·0.5M MgCl$_2$	0.50	67	2.30	"
80486-5	"	"	9.1	2M MgCl$_2$	0.17	78	1.90	

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